Nickel-Catalyzed Negishi Arylations of Propargylic Bromides: A Mechanistic Investigation

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Supporting Information

Table of Contents

I. General Information

The following reagents were purchased from commercial suppliers and used as received: Ph_2Zn, $NiBr_2$·DME, (–)-indanyl-pybox, (+)- and (–)-*i*-Pr-pybox, 4-fluorophenylmagnesium bromide, Cp^*_2Co, and $Ni(cod)_2$. (±)-(3-Bromohept-1-ynyl)trimethylsilane was prepared according to a literature procedure.[1] DME, THF, benzene, Et_2O, and toluene were degassed with argon and dried over activated alumina using a solvent purification system.

Elemental analyses were performed by Atlantic Microlab, Inc. and Midwest Microlab, LLC. Analysis of the enantioenriched organic products was conducted by GC using a chiral Supelco Beta-Dex-120 column. Yields by GC (FID detector) were determined with tetradecane as an internal standard.

Spectroscopy. UV–Vis measurements were taken with a Cary 50 UV–Vis spectrometer using either a 10 mm quartz cell or a 1.0 mm quartz cell. Measurements made below r.t. employed a Unisoku CoolSpeK cryostat. IR measurements were collected with NaCl plates on a Bio-Rad Excalibur FTS 3000 spectrometer. X-band EPR measurements were collected with a Bruker EMX spectrometer. EPR simulation was conducted using EasySpin.[2] NMR studies were performed on 400 and 500 MHz Varian spectrometers. ^{19}F NMR studies were conducted in a

(1) Smith, S. W.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 12645–12647.
(2) Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42–55.

mixture of DME/C_6D_6 and were referenced to a 4-fluorotoluene internal standard of known concentration (–118.9 ppm relative to $CFCl_3$ in DME/C_6D_6).

Cyclic Voltammetry. Cyclic voltammetry was performed using a 0.10 M solution of $TBAPF_6$ in THF in a glovebox under a nitrogen atmosphere. Electrochemical measurements were made with a CH Instruments 600B potentiostat using a standard three-electrode configuration. A glassy carbon electrode was used as the working electrode, and a platinum wire was used as the counter electrode. A silver wire in 0.10 M $TBAPF_6$ was used as the reference electrode. All potentials are reported relative to an internal ferrocene/ferrocenium reference.

Mass Spectrometry. ESI–MS experiments were conducted by direct injection using an LCQ ion trap mass spectrometer (Thermo). ESI–TOFMS experiments were conducted using an Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+) mode.

X-ray Crystallography. XRD studies were conducted at the Beckman Institute at Caltech using a Bruker SMART 1000 CCD and at the Stanford Synchrotron Radiation Lightsource (SSRL).

General Procedure for stoichiometric arylations of propargylic bromides. In a nitrogen-filled glovebox, a solution of [((–)-*i*-Pr-pybox)NiPh]BAr^F_4 (37.5 mg, 0.029 mmol) in DME (4.5 mL) was treated with a solution of the propargylic bromide (7.5 mg, 0.030 mmol) in DME (2.0 mL) at r.t. At the appropriate time, an aliquot was removed, passed through a plug of silica gel, and analyzed by GC. The initial concentration of nickel under these conditions is equal to the concentration of nickel in catalytic reactions conducted according to the general procedure below.

General Procedure for catalytic arylations of propargylic bromides. In a nitrogen-filled glovebox, a solution of the diarylzinc (0.11 mmol) in DME (0.28 mL) was added to a 4 mL vial fitted with a PTFE septum cap. This solution was placed in a –20 °C bath, and then it was treated with a solution of the nickel complex (0.0021 mmol) in DME (0.20 mL) followed immediately by the neat propargylic bromide (17.5 mg, 0.071 mmol). After 17 h at –20 °C, the solution was treated with ethanol (0.1 mL) in Et_2O (0.4 mL), passed through a plug of silica gel, and analyzed by GC.

General Procedure for monitoring catalytic reactions by ^{19}F NMR spectroscopy. A solution of the bis(4-fluorophenyl)zinc (28.4 mg, 0.11 mmol) in DME (0.22 mL) was placed in a screw-cap NMR tube fitted with a PTFE septum cap. A solution of the internal standard (4-fluorotoluene) in C_6D_6 (0.050 mL) was then added. The probe was cooled to –20 °C, and the NMR sample (pre-cooled to –40 °C) was treated sequentially with the neat propargylic bromide (17.5 mg, 0.071 mmol) and then a solution of (*i*-Pr-pybox)$NiBr_2$ in DME (0.20 mL). The cold sample was quickly transferred to the NMR probe. All NMR yields are reported relative to the internal standard.

II. Synthesis and Characterization

These yields have not been optimized.

Bis(4-fluorophenyl)zinc. The title compound was prepared by an adaptation of a literature procedure.[3] 4-Fluorophenylmagnesium bromide (8.5 mL, 17 mmol; 2.0 M solution in Et_2O) was added to dry $ZnBr_2$ (1.89 g, 8.4 mmol, 0.49 equiv) in Et_2O (3.0 mL) at r.t., and the resulting solution was stirred for 16 h at r.t. Next, 1,4-dioxane (1.8 mL) was added, furnishing a suspension, which was filtered and washed with excess Et_2O under nitrogen. The combined washings were evaporated to dryness, and the resulting solid was sublimed at 105 °C under vacuum (~0.3 torr) onto a water-chilled cold finger to give the product as a colorless, microcrystalline solid. Yield 1.0 g (47%).

((–)-*i*-Pr-pybox)$Ni^{II}Br_2$.[4] (–)-*i*-Pr-pybox (1.67 g, 5.54 mmol) and $NiBr_2$·DME (1.72 g, 5.56 mmol) were weighed in the air and added to a 250 mL Schlenk flask under nitrogen. Dry, degassed THF (80 mL) was then added, and the mixture was heated to 65 °C for 4 h. Next, the heating bath was removed, and the warm solution was decanted under N_2 into a 100 mL Schlenk flask, using a filter cannula. Upon cooling, a solid formed. The flask was maintained at 0 °C in an ice bath for 2 h, and then the cold supernatant was removed using a filter cannula. The resulting solid was washed with Et_2O (20 mL x 2) and then dried under vacuum. Yield: 2.19 g (76%).

^{1}H NMR (400 MHz, THF-d_8) δ 66.50 (s, 2H), 37.54 (s, 2H), 17.33 (s, 3H), 11.92 (s, 2H), 8.58 (s, 2H), 4.72 (s, 6H), 4.18 (s, 6H). This is a high-spin Ni(II) complex.

Calculated for $C_{17}H_{23}Br_2N_3NiO_2$: C, 39.27; H, 4.46; N, 8.08. Found: C, 39.36; H, 4.53; N, 8.15.

((–)-*i*-Pr-pybox)$Ni^{I}Br$.[4] In a glovebox, (–)-*i*-Pr-pybox (0.148 g, 0.491 mmol) and $Ni(cod)_2$ (67.6 mg, 0.246 mmol) were combined in a round bottom flask with dry, deoxygenated THF (20 mL). The mixture was stirred for 10 min, and then $NiBr_2$·DME (0.0756 g, 0.245 mmol) was added in one portion. The resulting purple solution was stirred for one hour at r.t., and then it was treated with pentane (10 mL) and stored at –40 °C overnight. Next, the cold solution was vacuum filtered in the glovebox, giving a purple solid, which was washed with hexanes and dried under vacuum. The product is air-sensitive both in solution and as a solid. Yield: 0.202 g (94%).

^{1}H NMR (400 MHz, THF-d_8) δ 9.62 (br), 2.37 (br), 0.35 (br). This is a paramagnetic Ni(I) complex.

Calculated for $C_{17}H_{23}BrN_3NiO_2$: C, 46.41; H, 5.27; N, 9.55. Found: C, 46.29; H, 5.17; N, 9.37.

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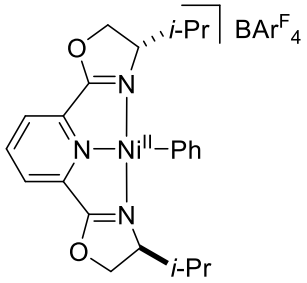
(3) Kimura, M.; Tatsuyama, Y.; Kojima, K.; Tamaru, Y. *Org. Lett.* **2007**, *9*, 1871–1873.

(4) This compound was first prepared by Trixia M. Buscagan.



[((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^F_4$ (1). In a glovebox, ((–)-*i*-Pr-pybox)NiBr$_2$ (0.603 g, 1.16 mmol) was combined with THF (25 mL). The resulting slurry was cooled to –45 °C in a cold well, and a solution of Ph_2Zn (0.128 g, 0.583 mmol) in THF (2.0 mL) was added dropwise over 0.5 min. The reaction mixture was stirred for two additional minutes, and then a solution of NaBAr$^F_4$ (1.08 g, 1.22 mmol) in THF (8.0 mL) was added in one portion. The resulting deep-red solution was maintained at –45 °C for 5 min, stirring periodically. Next, it was passed through a 1" plug of dry, basic alumina through which THF had already been passed. The alumina was washed with THF (10 mL x 2), and these THF washings were concentrated to dryness under vacuum. The red residue was washed with pentane (20 mL x 2), and then it was extracted with toluene (50 mL x 3). The combined toluene extracts were filtered and then evaporated to dryness, leaving the product as a red, microcrystalline solid. Yield: 1.06 g (70%).

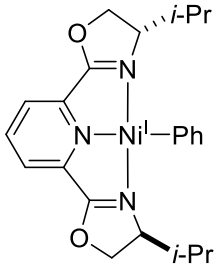
Crystals suitable for X-ray crystallography were obtained by cooling a saturated solution in benzene.

^{1}H NMR (400 MHz, THF-d_8) δ 8.42 (t, J = 7.9 Hz, 1H), 8.09 (d, J = 8.0 Hz, 2H), 7.79 (s, 8H), 7.57 (s, 4H), 7.40 (d, J = 7.4 Hz, 2H), 7.01 (t, J = 7.4 Hz, 2H), 6.93 (t, J = 7.3 Hz, 1H), 4.96–4.92 (m, 4H), 4.10–3.86 (m, 2H), 1.15–1.03 (m, 2H), 0.74 (d, J = 6.9 Hz, 6H), 0.53 (d, J = 7.1 Hz, 6H).

^{13}C NMR (101 MHz, THF-d_8) δ 169.8, 162.9 (q, J = 49.9 Hz), 144.0, 143.6, 141.9, 136.9, 135.6, 130.3–129.8 (m), 127.6, 125.6 (q, J = 272.2 Hz), 125.53, 125.52, 118.4–118.0 (m), 75.7, 66.4, 29.4, 18.3, 13.8.

$[\alpha]_D^{25}$ = +46 (c 0.11, THF; (*S,S*)-enantiomer).

Calculated for $C_{55}H_{40}BF_{24}N_3NiO_2$: C, 50.80; H, 3.10; N, 3.23. Found: C, 50.96; H, 3.19; N, 3.21.

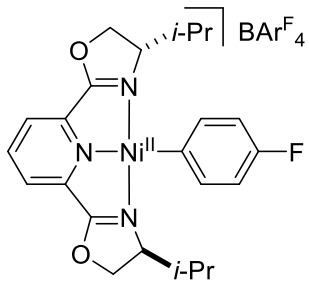


((–)-*i*-Pr-pybox)Ni^{I}Ph (2). In a glovebox, [((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^F_4$ (**1**; 0.158 g, 0.122 mmol) was dissolved in dry, degassed Et_2O (5.0 mL), and the resulting mixture was cooled to –40 °C in a cold well. Solid Cp^*_2Co (0.0340 g, 0.103 mmol) was finely ground with a magnetic stir bar and then dissolved in Et_2O (2.0 mL). This solution was then added to the solution of the nickel complex. The reaction vessel was maintained at –40 °C for 30 min, and then the mixture

was evaporated to dryness at –40 °C under vacuum. The residue was extracted with tetramethylsilane at 0 °C (10 mL x 4), and the combined extracts were filtered through a PTFE syringe filter and evaporated to dryness under vacuum at –40 °C to give the product as a dark solid. Yield: 0.020 g (44%).

Crystals suitable for X-ray crystallography were obtained by concentration of the cold tetramethylsilane solution under vacuum.

Calculated for $C_{23}H_{28}N_3NiO_2$: C, 63.19; H, 6.46; N, 9.61. Found: C, 62.79; H, 6.31; N, 9.22.



[((–)-*i*-Pr-pybox)Ni^{II}(C_6H_4F)]BAr$^F_4$ (4). In a glovebox, ((–)-*i*-Pr-pybox)$NiBr_2$ (0.405 g, 0.779 mmol) was combined with THF (15 mL). The resulting slurry was cooled to –78 °C in a cold well, and then $(C_6H_4F)_2Zn$ (0.0997 g, 0.390 mmol) was added. After 1 min, a solution of $NaBAr^F_4$ (0.720 g, 0.812 mmol) in Et_2O (4 mL) was added in one portion. The resulting deep-red solution was maintained at –78 °C for 5 min, stirring periodically. Next, it was passed through a 1" plug of dry, basic alumina through which Et_2O had already been passed. The alumina was washed with Et_2O (60 mL), and the resulting solution was reduced to dryness under vacuum. The residue was washed with pentane (10 mL x 2), and then it was extracted with toluene (75 mL x 2). The combined toluene extracts were filtered and then evaporated to dryness, providing an oily residue that was washed with pentane (20 mL) and then dried under vacuum. Addition of Et_2O (5 mL) furnished a deep-red solution, which was reduced to dryness under vacuum to yield a solid, transferrable foam. Yield: 0.594 g (58%).

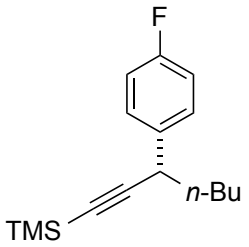
Calculated for $C_{55}H_{39}BF_{25}N_3NiO_2$: C, 50.11; H, 2.98; N, 3.19. Found: C, 50.00; H, 3.02; N, 3.15.

^{1}H NMR (400 MHz, THF-d_8) δ 8.43 (t, J = 8.0 Hz, 1H), 8.09 (d, J = 7.7 Hz, 2H), 7.80 (s, 8H), 7.58 (s, 4H), 7.39 (t, J = 6.9 Hz, 2H), 6.90 (t, J = 8.8 Hz, 2H), 4.96–4.86 (m, 4H), 4.06–3.86 (m, 2H), 1.08 (m, 2H), 0.74 (d, J = 6.8 Hz, 6H), 0.56 (d, J = 7.0 Hz, 6H).

^{13}C NMR (101 MHz, THF-d_8) δ 170.0, 163.4 (d, J = 242.0 Hz), 162.9 (q, J = 49.9 Hz), 144.2, 143.6, 137.2 (d, J = 5.8 Hz), 135.7, 133.6, 130.4–129.8 (m), 125.7, 125.6 (q, J = 272.2 Hz), 118.6–117.9 (m), 114.6 (d, J = 19.1 Hz), 75.7, 66.4, 29.6, 18.3, 13.8.

^{19}F NMR (376 MHz, THF-d_8) δ –63.47 (s), –121.28 (m).

^{19}F NMR (470 MHz, C_6D_6 in DME, –20 °C) δ –62.33 (s), –120.47 (m).



(*S*)-(3-(4-fluorophenyl)-1-heptynyl)trimethylsilane. The title compound was synthesized from (±)-(3-bromohept-1-ynyl)trimethylsilane by the General Procedure for catalytic arylations of propargylic bromides, with ((+)-*i*-Pr-pybox)$NiBr_2$ as the precatalyst. The product was purified by chromatography (100% hexanes), which furnished a colorless oil.

^{1}H NMR (500 MHz, C_6D_6) δ 7.14–7.06 (m, 2H), 6.83–6.73 (m, 2H), 3.47 (dd, *J* = 8.3, 6.1 Hz, 1H), 1.72–1.62 (m, 1H), 1.61–1.51 (m, 1H), 1.47–1.26 (m, 2H), 1.24–1.12 (m, 2H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.21 (s, 9H).

^{13}C NMR (126 MHz, C_6D_6) δ 162.2 (d, *J* = 244.5 Hz), 138.0 (d, *J* = 3.0 Hz), 129.3 (d, *J* = 7.9 Hz), 115.5 (d, *J* = 21.4 Hz), 109.1, 87.5, 38.6, 38.5, 29.8, 22.7, 14.1, 0.3.

^{19}F NMR (470 MHz, C_6D_6) δ –116.35 (m).

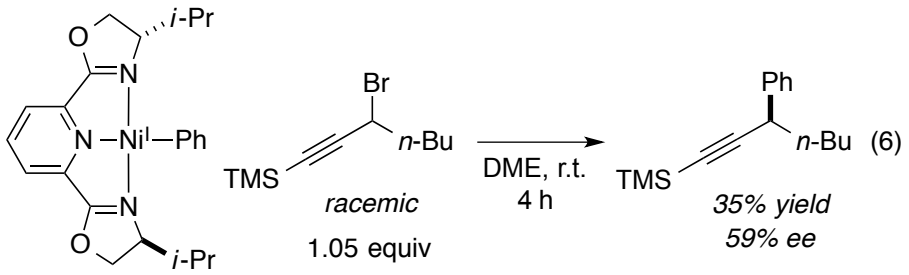
^{19}F NMR (470 MHz, C_6D_6 in DME, –20 °C) δ –116.97 (m).

FT-IR (neat) 2959, 2934, 2861, 2172, 1605, 1509, 1250, 1227, 1158, 910, 842, 760 cm^{-1}.

MS (EI) *m*/*z* (M^+) calculated for $C_{16}H_{23}FSi$: 262.2, found: 262.3.

$[\alpha]_D^{25}$ = −10.5 (c 0.49, $CHCl_3$; (*S*)-enantiomer, 83% ee).

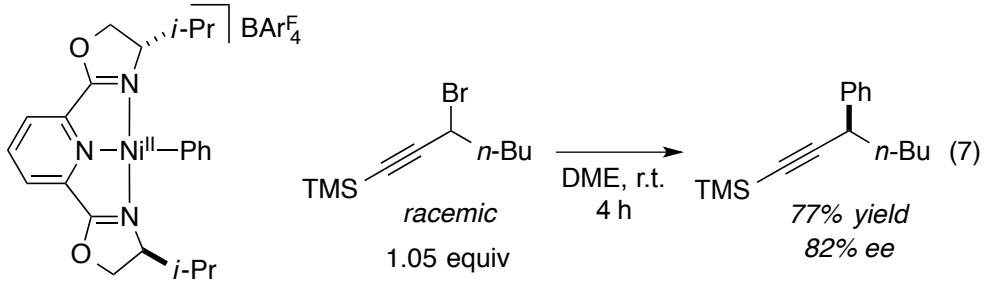
III. Mechanistic Studies



2

Stoichiometric reaction of ((–)-*i*-Pr-pybox)Ni^{I}Ph with a propargylic bromide (eq 6). In a nitrogen-filled glovebox, ((–)-*i*-Pr-pybox)NiPh (9.0 mg, 0.021 mmol) was dissolved in DME (3.9 mL), and then a solution of (±)-(3-bromohept-1-ynyl)trimethylsilane (5.4 mg, 0.022 mmol) in DME (0.71 mL) was added in one portion with rapid stirring. After 4 h at r.t., an aliquot was removed, passed through a plug of silica gel, and analyzed by GC. Calibrated GC yield: 35% (59% ee).

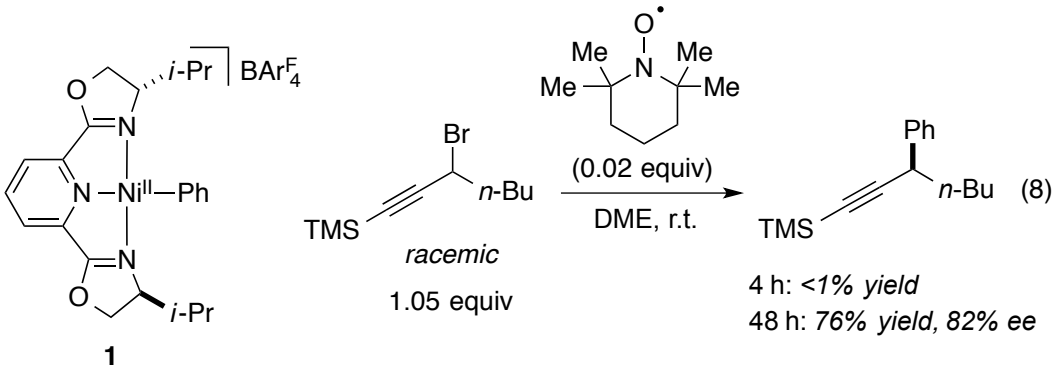
An aliquot removed after 20 min and analyzed by EPR spectroscopy was found to be EPR-silent.



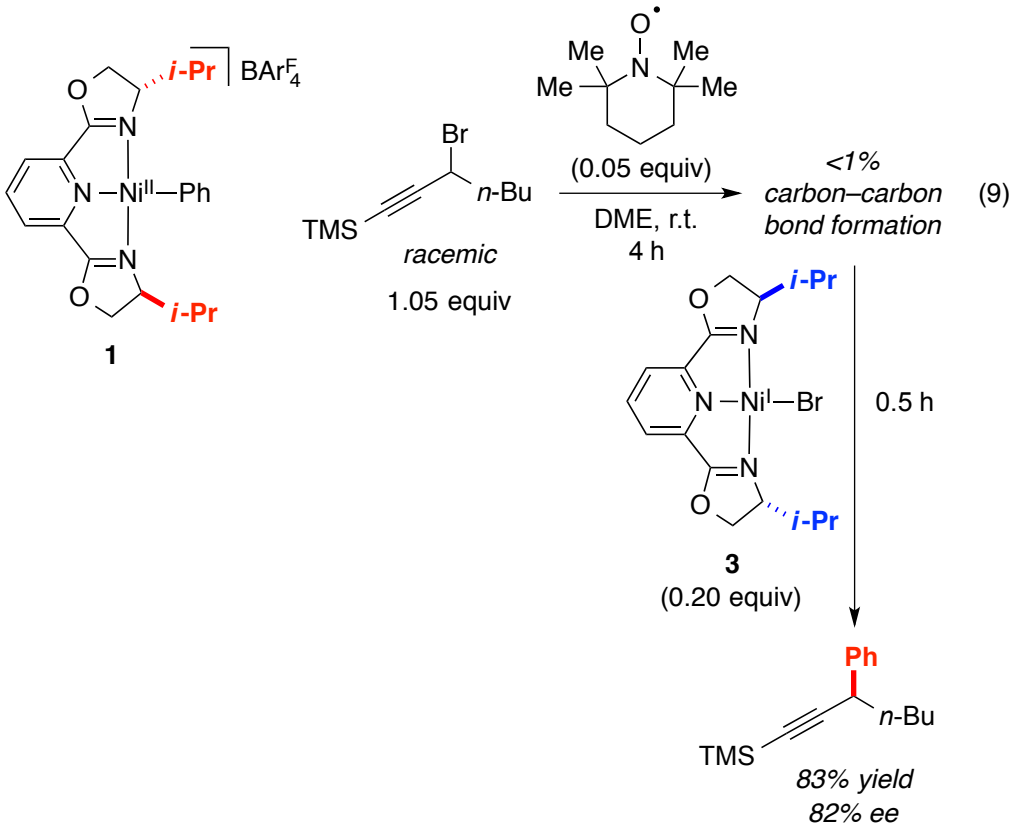
1

Stoichiometric reaction of [((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^{F}_{4}$ with a propargylic bromide (eq 7). This experiment was set up according to the General Procedure for stoichiometric arylations of propargylic bromides. Calibrated GC yield after 4 h: 77% (82% ee).

An aliquot removed after 20 min and analyzed by EPR spectroscopy was found to be EPR-silent.

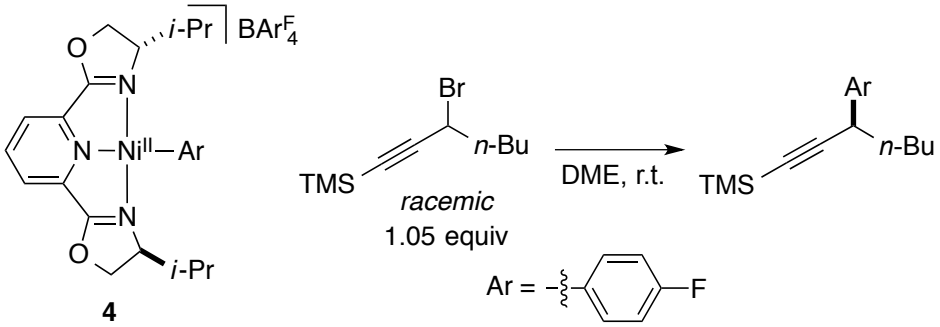


Stoichiometric reaction of [((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^F_4$ with a propargylic bromide in the presence of TEMPO (eq 8). This experiment was set up according to the General Procedure for stoichiometric arylations of propargylic bromides, except that a solution of TEMPO in DME (17.2 μL of a 5.2 mg/mL solution; 0.090 mg, 0.57 μmol, 0.020 equiv) was added immediately prior to the addition of the propargylic bromide. Calibrated GC yield after 4 h: <1%. Calibrated GC yield after 48 h: 76% (82% ee).



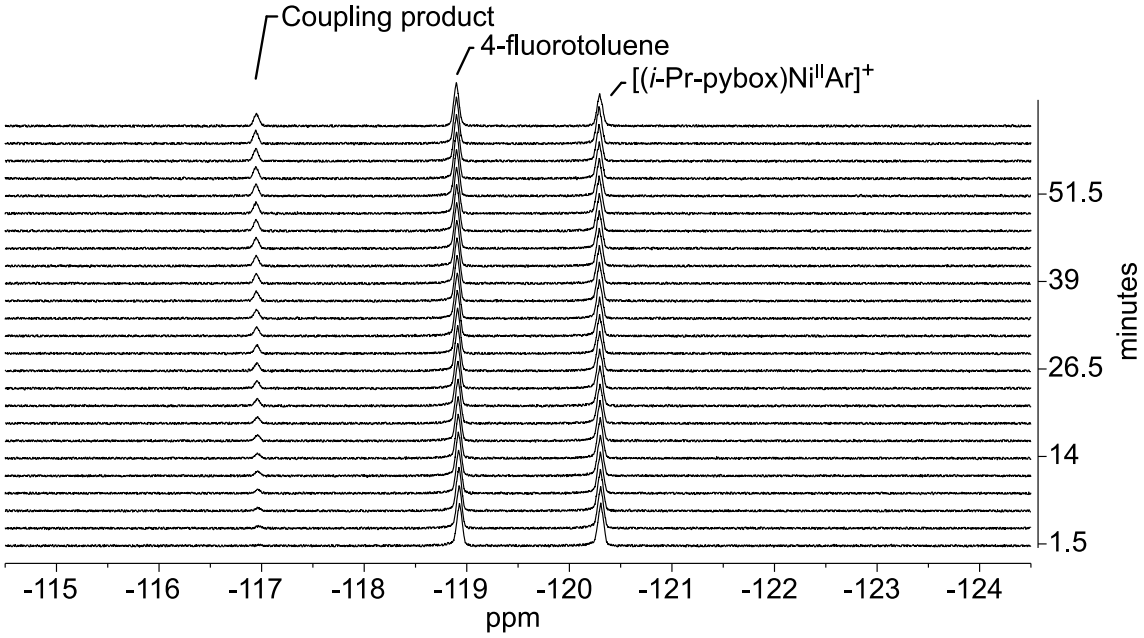
Initiation by ((+)-*i*-Pr-pybox)Ni^{I}Br of a TEMPO-inhibited stoichiometric arylation (eq 9). This experiment was set up according to the General Procedure for stoichiometric arylations of propargylic bromides, except that a solution of TEMPO in DME (45.0 μL of a 5.2 mg/mL solution; 0.23 mg, 1.5 μmol, 0.052 equiv) was added immediately prior to the addition of the propargylic bromide. After 4 h at r.t., an aliquot was removed, passed through a plug of silica gel, and analyzed by GC, which showed that there was <1 % of the coupling product.

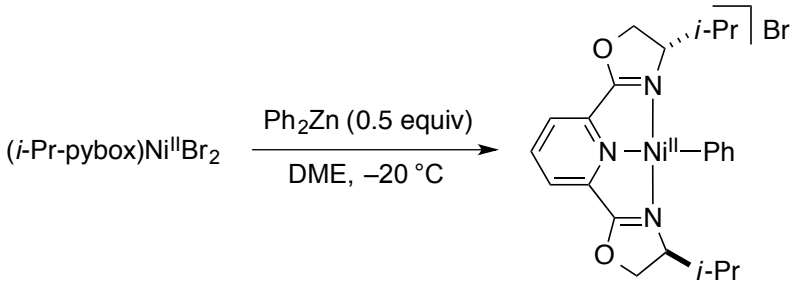
A solution of ((+)-*i*-Pr-pybox)Ni^{I}Br (2.5 mg, 5.8 μmol, 0.20 equiv) in DME (0.53 mL) was then added, with vigorous stirring. Analysis of an aliquot removed after an additional 0.5 h showed that the reaction had proceeded to completion. Calibrated GC yield: 83% (82% ee).



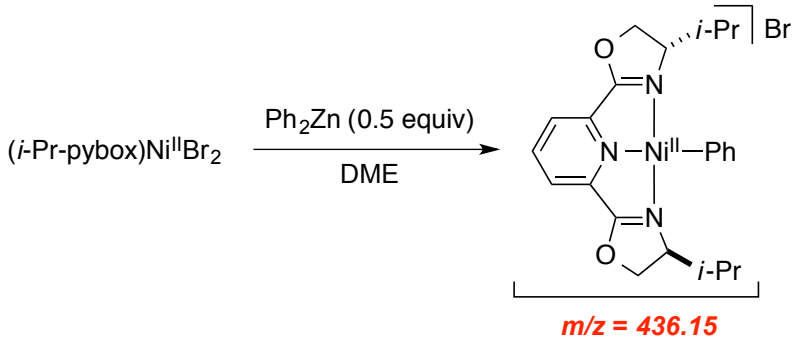
4

Progress of a stoichiometric reaction of [((–)-*i*-Pr-pybox)Ni^{II}(C$_6$H$_4$F)]BAr$^F_4$ with a propargylic bromide (Figure 5). A solution formed by mixing [((–)-*i*-Pr-pybox)Ni(C$_6$H$_4$F)]BAr$^F_4$ (0.029 mmol) in DME (0.42 mL) with the internal standard (4-fluorotoluene) in C$_6$D$_6$ (0.050 mL) was treated with (±)-(3-bromohept-1-ynyl)trimethylsilane (0.030 mmol). The progress of this reaction was followed by ^{19}F NMR spectroscopy over 60 min.

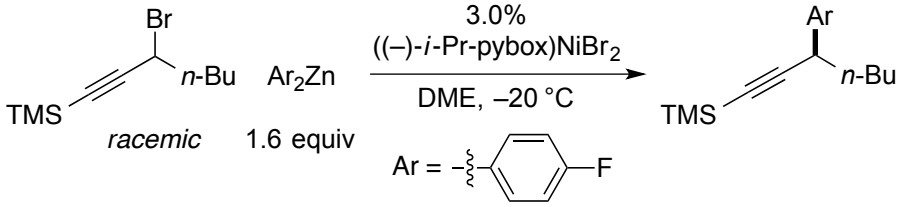




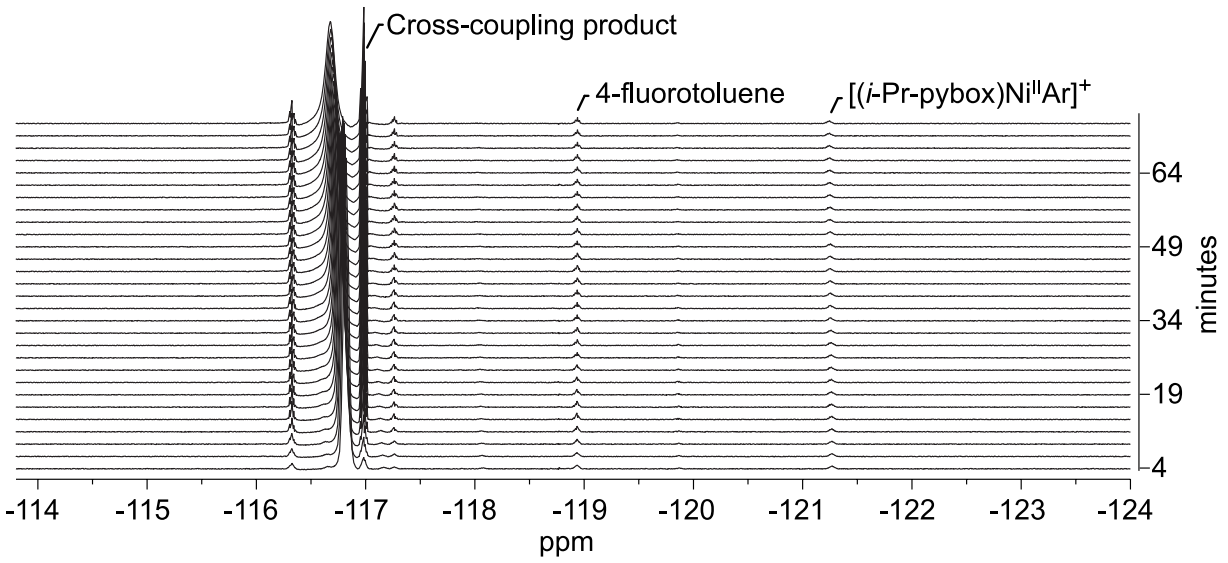
Analysis via UV–Vis spectroscopy of the reaction of ((–)-*i*-Pr-pybox)Ni^{II}Br$_2$ with Ph$_2$Zn to form [(*i*-Pr-pybox)Ni^{II}Ph]$^+$ (Figure 7). A 10 mm quartz UV–Vis cuvette equipped with a magnetic stir bar was charged with a solution of ((–)-*i*-Pr-pybox)NiBr$_2$ in DME (0.45 mM; 3.45 mL, 1.5 μmol), sealed with a PTFE septum cap, and cooled to –20 °C in the spectrometer. A solution of Ph$_2$Zn in DME (12 μL of a 14.2 mg/mL solution; 0.17 mg, 0.78 μmol, 0.50 equiv) was then added, and the reaction was monitored by UV–Vis spectroscopy at –20 °C.

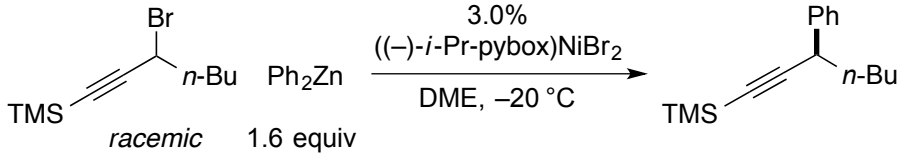


Analysis via ESI–MS (positive-ion mode) of the reaction of (*i*-Pr-pybox)Ni^{II}Br$_2$ with Ph$_2$Zn to form [(*i*-Pr-pybox)Ni^{II}Ph]$^+$ (Figure 8). A dry vial was charged with a solution of ((–)-*i*-Pr-pybox)NiBr$_2$ in DME (0.45 mM; 3.45 mL, 1.5 μmol), sealed with a PTFE septum cap, and cooled in a –78 °C bath. A solution of Ph$_2$Zn in DME (12 μL of a 14.2 mg/mL solution; 0.17 mg, 0.78 μmol, 0.50 equiv) was added, and then the vial was removed from the bath. An aliquot was removed using a microsyringe and immediately analyzed by ESI–MS (positive-ion mode) at r.t.

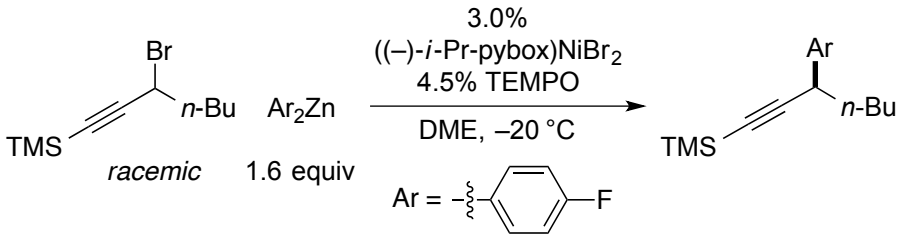


Analysis via ^{19}F NMR spectroscopy of a catalyzed Negishi reaction in progress (Figure 9). This experiment was set up according to the General Procedure for monitoring catalytic reactions by ^{19}F NMR spectroscopy.

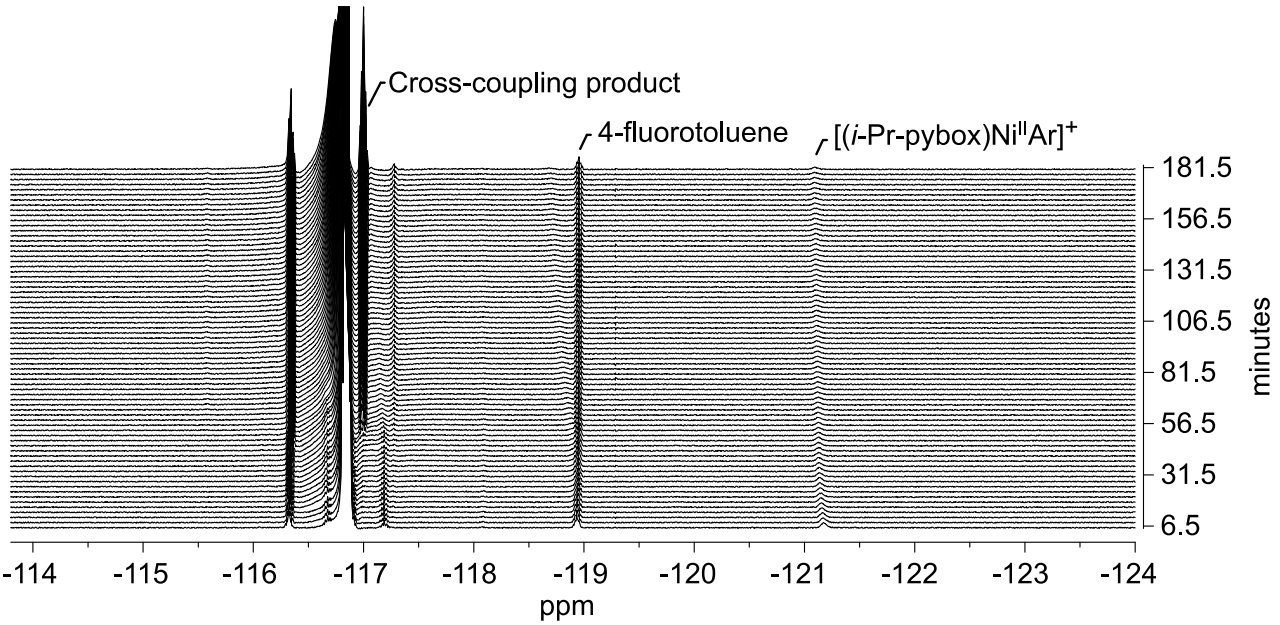




Analysis via UV–Vis spectroscopy of a catalyzed Negishi reaction in progress (Figure 10). A 1.0 mm quartz UV–Vis cuvette (total volume: 350 μL) was charged with a solution of Ph_2Zn (0.0185 g, 0.084 mmol) in DME (0.20 mL) and then (±)-(3-bromohept-1-ynyl)trimethylsilane (0.0129 g, 0.052 mmol). The solution was cooled to –20 °C in the spectrometer, and then a solution of ((–)-*i*-Pr-pybox)$NiBr_2$ (0.80 mg in DME (0.15 mL), 1.5 μmol) was added. The reaction was monitored from 800 to 300 nm at a rate of 1200 nm/min with one scan collected every 30 s.

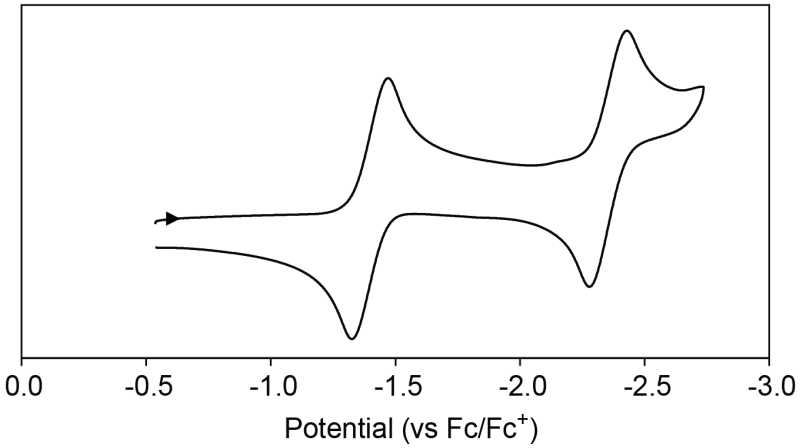


Analysis via ^{19}F NMR spectroscopy of a catalyzed Negishi reaction in progress, in the presence of TEMPO (Figure 11). This experiment was set up according to the General Procedure for monitoring catalytic reactions by ^{19}F NMR spectroscopy, with the following modification: the diarylzinc was dissolved in 0.13 mL, instead of 0.22 mL, of DME; a solution of TEMPO in DME (93.0 μL of a 5.2 mg/mL solution; 0.48 mg, 0.0031 mmol, 0.045 equiv) was added immediately prior to the addition of the solution of the nickel complex.

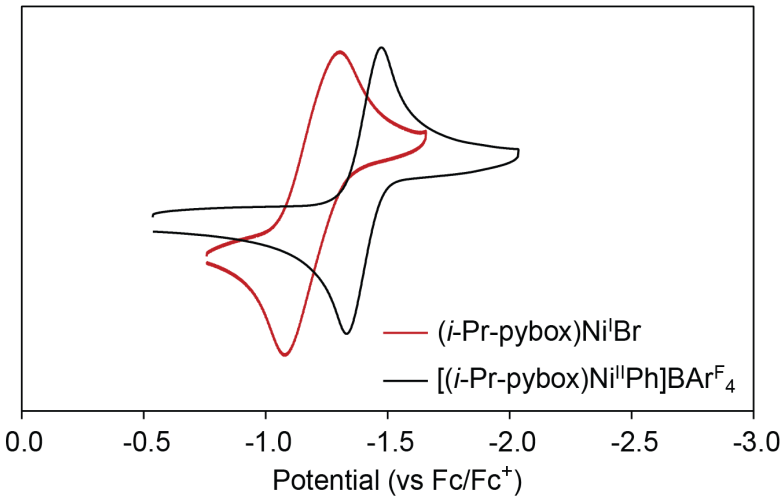

Cross-coupling product
4-fluorotoluene
[(i-Pr-pybox)Ni^II Ar]^+
181.5
156.5
131.5
106.5
81.5
56.5
31.5
6.5
minutes
-114
-115
-116
-117
-118
-119
-120
-121
-122
-123
-124
ppm

IV. Cyclic Voltammetry Data

Cyclic Voltammagram of [((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^{F}_{4}$ in THF (100 mV/s, 0.10 M TBAPF$_6$).

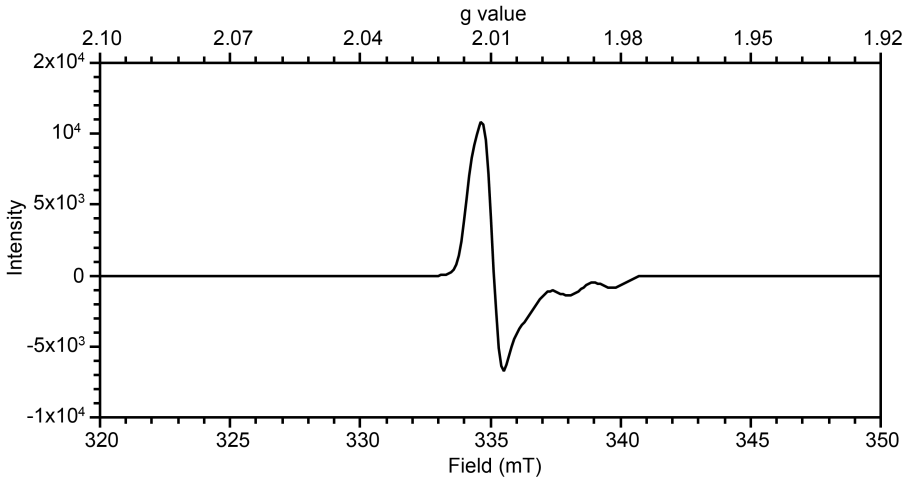


Cyclic Voltammagram of [(*i*-Pr-pybox)Ni^{II}Ph]BAr$^{F}_{4}$ overlaid with (*i*-Pr-pybox)Ni^{I}Br in THF (100 mV/s, 0.10 M TBAPF$_6$, arbitrary *y* scale).



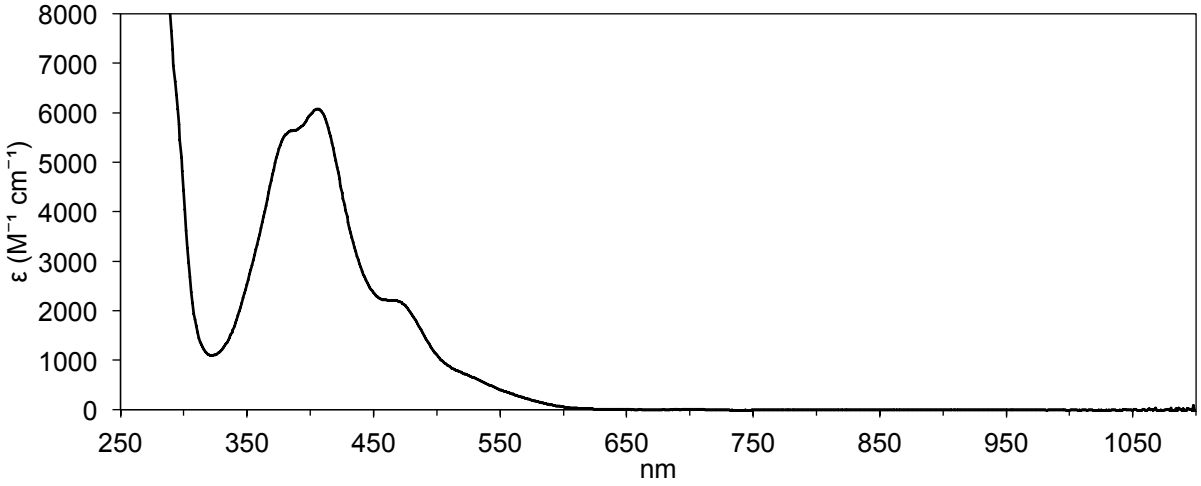
V. EPR Data

X-band EPR spectrum of (*i*-Pr-pybox)Ni^{I}Ph (toluene, 77 K)

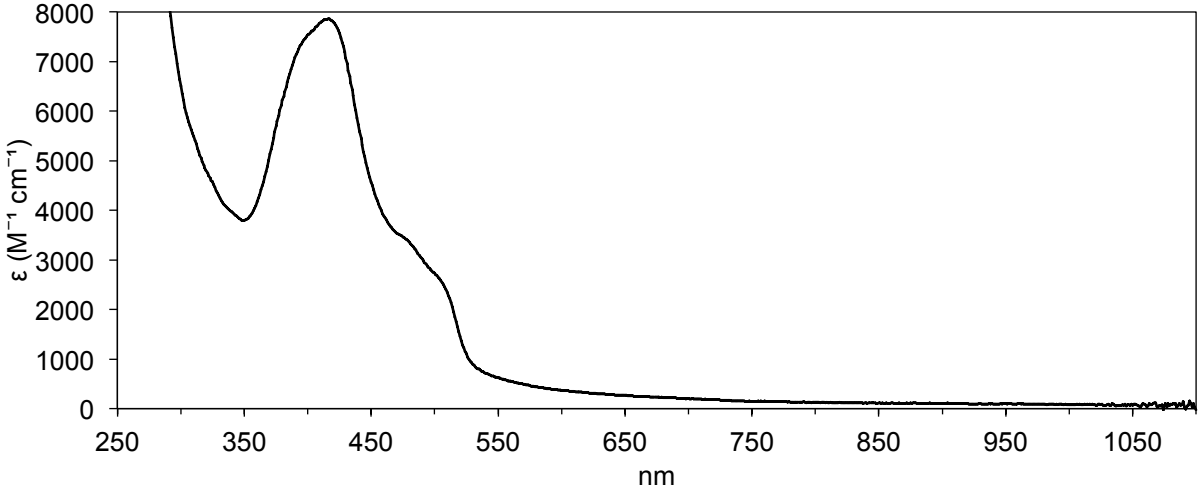


VI. UV–Visible Spectra

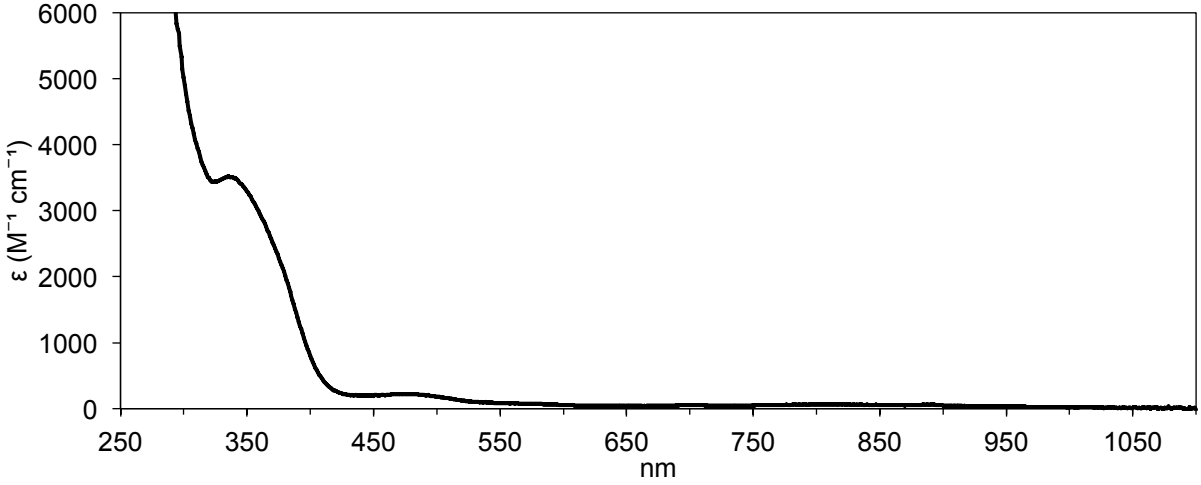
UV–Vis of [((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^{F}_{4}$ (DME, –20 °C)



UV–Vis of ((–)-*i*-Pr-pybox)Ni^{I}Ph (DME, –20 °C)



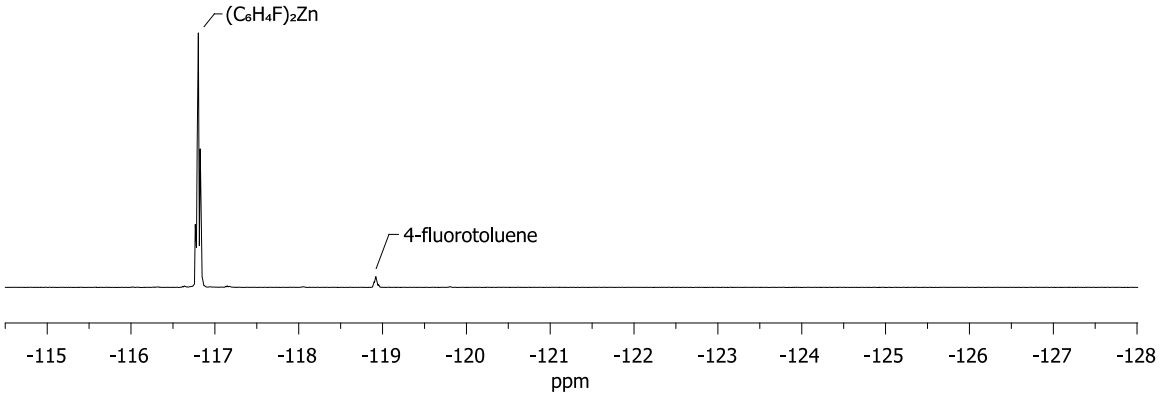
UV–Vis of ((–)-*i*-Pr-pybox)Ni^{II}Br$_2$ (DME, –20 °C)



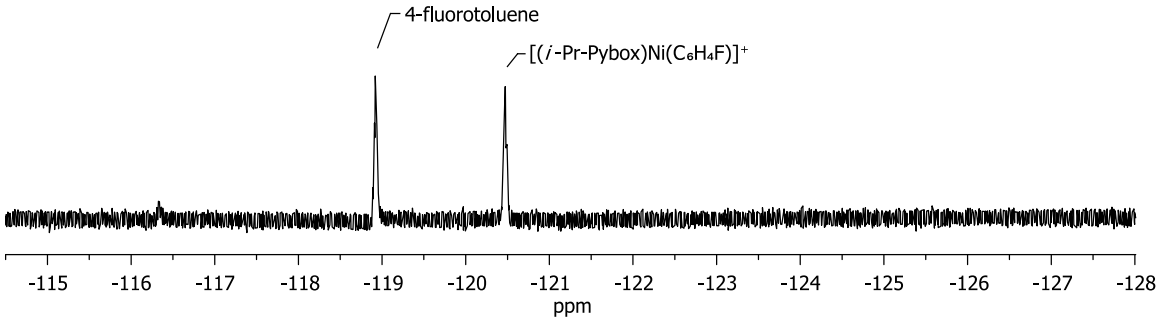
VII. ^{19}F NMR Spectra

Conditions: DME (425 μL) and C_6D_6 (50 μL) at –20 °C, with 4-fluorotoluene (4.3 mM) as an internal standard (–118.92 ppm).

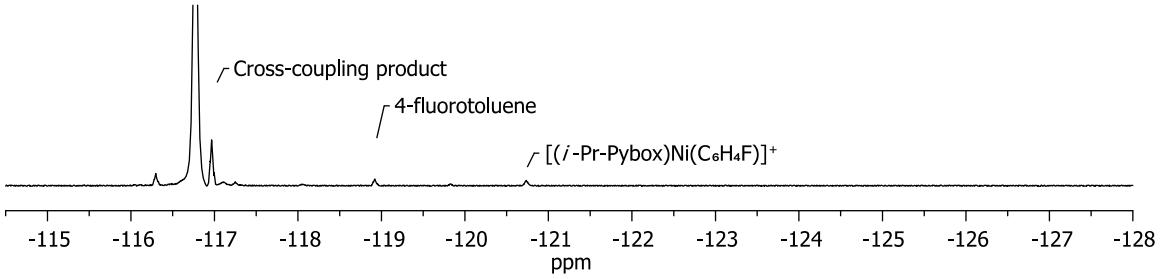
^{19}F NMR of $(C_6H_4F)_2Zn$



^{19}F NMR of [((–)-*i*-Pr-pybox)Ni^{II}(C_6H_4F)]BAr^F_4

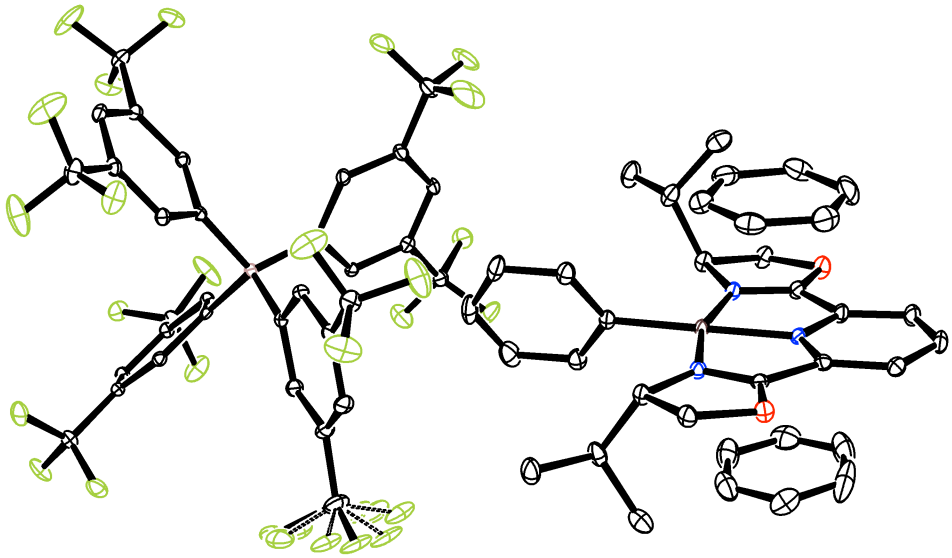


^{19}F NMR analysis of a catalyzed Negishi reaction with added $NaBAr^F_4$. This experiment was set up according to the General Procedure for monitoring catalytic reactions by ^{19}F NMR spectroscopy, except that $NaBAr^F_4$ (5.6 mg, 0.0067 mmol, 0.096 equiv) was added to the solution of the organozinc reagent. The following spectrum was collected after 20 min.



VIII. X-Ray Crystallographic Data

[((–)-*i*-Pr-pybox)Ni^{II}Ph]BAr$^{F}_{4}$ (1). A suitable crystal of $C_{55}H_{40}N_3NiO_2BF_{24}\cdot 2(C_6H_6)$ was selected for analysis and mounted in a nylon loop. All measurements were made on a Bruker SMART 1000 CCD with filtered Mo–Kα radiation at a temperature of 100 K. Using Olex2, the structure was solved with the ShelXS[5] structure solution program using Direct Methods and refined with the ShelXL[6] refinement package using Least Squares minimization. Three-site rotational disorder in one trifluoromethyl group of the anion was modeled with the appropriate similarity restraints. The absolute stereochemistry was determined on the basis of the known stereochemistry of the commercially available ligand and the absolute structure parameter.



ORTEP diagram of the asymmetric unit with ellipsoids shown at 30% probability

(5) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

(6) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112–122.

Table S–1. Crystal data and structure refinement for crystal01.

Identification code	[((–)-*i*-Pr-pybox)NiPh]$BAr^{F}{}_{4}$	
Empirical formula	$C_{55}H_{40}N_3NiO_2BF_{24}\cdot 2(C_6H_6)$	
Formula weight	1456.63	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 13.0108(13) Å	α = 90°.
	b = 13.0547(13) Å	β = 90°.
	c = 37.484(4) Å	γ = 90°.
Volume	6366.8(11) $Å^3$	
Z	4	
Density (calculated)	1.520 Mg/m^3	
Absorption coefficient	0.423 mm^{-1}	
F(000)	2960	
Crystal size	0.3 x 0.15 x 0.15 mm^3	
Theta range for data collection	1.652 to 27.673°.	
Index ranges	-16<=h<=16, -16<=k<=16, -48<=l<=48	
Reflections collected	79002	
Independent reflections	14748 [R(int) = 0.0552]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9023	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14748 / 85 / 944	
Goodness-of-fit on F^2	1.026	
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0777	
R indices (all data)	R1 = 0.0568, wR2 = 0.0848	
Absolute structure parameter	-0.017(4)	
Largest diff. peak and hole	0.395 and -0.283 $e/Å^{-3}$	

Table S–2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal01. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni(1)	1996(1)	4994(1)	6166(1)	16(1)
O(1)	-64(2)	3278(2)	6660(1)	26(1)
O(2)	4215(2)	6562(2)	6637(1)	22(1)
N(1)	886(2)	4086(2)	6246(1)	19(1)
N(2)	2078(2)	4922(2)	6671(1)	17(1)
N(3)	3136(2)	5876(2)	6234(1)	18(1)
C(1)	145(3)	3498(3)	6030(1)	22(1)
C(2)	-600(3)	3099(3)	6319(1)	26(1)
C(3)	719(3)	3884(3)	6578(1)	21(1)
C(4)	1415(3)	4327(3)	6845(1)	21(1)
C(5)	1474(3)	4218(3)	7213(1)	26(1)
C(6)	2244(3)	4749(3)	7389(1)	27(1)
C(7)	2932(3)	5367(3)	7206(1)	23(1)
C(8)	2818(2)	5432(2)	6838(1)	18(1)
C(9)	3409(2)	5979(2)	6562(1)	17(1)
C(10)	4624(3)	6877(3)	6289(1)	23(1)
C(11)	3826(3)	6504(3)	6012(1)	20(1)
C(12)	700(3)	2664(3)	5815(1)	27(1)
C(13)	1187(3)	1846(3)	6049(1)	36(1)
C(14)	-27(4)	2204(3)	5540(1)	40(1)
C(15)	3243(3)	7341(3)	5813(1)	28(1)
C(16)	3930(4)	7854(3)	5537(1)	42(1)
C(17)	2757(3)	8120(3)	6063(1)	34(1)
C(18)	1920(2)	5051(2)	5665(1)	19(1)
C(19)	1097(3)	5537(3)	5497(1)	26(1)
C(20)	1042(3)	5598(3)	5129(1)	36(1)
C(21)	1796(3)	5170(3)	4922(1)	38(1)
C(22)	2612(3)	4679(3)	5079(1)	33(1)
C(23)	2676(3)	4622(3)	5451(1)	25(1)
F(1)	1546(2)	8730(2)	3076(1)	29(1)
F(2)	578(2)	8449(2)	2622(1)	32(1)
F(3)	2130(2)	7878(2)	2631(1)	34(1)
F(4)	-2114(2)	5941(2)	3095(1)	39(1)
F(5)	-1522(2)	5287(2)	2618(1)	26(1)
F(6)	-1538(2)	4393(2)	3094(1)	49(1)
F(7)	5540(2)	5439(2)	4344(1)	51(1)

F(8)	4906(2)	5542(2)	4865(1)	54(1)
F(9)	5574(2)	6852(2)	4621(1)	46(1)
F(10)	2655(7)	9100(6)	4631(2)	41(2)
F(10A)	2907(13)	9186(13)	4496(4)	40(2)
F(10B)	2108(11)	9128(12)	4181(4)	41(2)
F(11)	1868(9)	9052(11)	4118(4)	33(2)
F(11A)	1523(13)	8860(13)	4213(5)	41(2)
F(11B)	958(9)	8367(10)	4473(3)	41(2)
F(12)	1175(10)	8354(10)	4577(3)	45(2)
F(12A)	1647(13)	8385(11)	4747(4)	43(2)
F(12B)	2295(7)	8869(7)	4752(2)	41(2)
F(13)	-1116(2)	4520(2)	4818(1)	40(1)
F(14)	-1678(2)	3195(2)	4544(1)	31(1)
F(15)	-1665(2)	4648(2)	4280(1)	40(1)
F(16)	2550(2)	1403(2)	4232(1)	50(1)
F(17)	2602(2)	2053(2)	4752(1)	70(1)
F(18)	1348(2)	1099(2)	4604(1)	50(1)
F(19)	1824(2)	2404(2)	2680(1)	36(1)
F(20)	2608(2)	1438(2)	3048(1)	34(1)
F(21)	3373(2)	1925(2)	2576(1)	57(1)
F(22)	5897(2)	5248(2)	3350(1)	38(1)
F(23)	5434(2)	5589(2)	2818(1)	55(1)
F(24)	6119(2)	4143(2)	2936(1)	59(1)
C(24)	1213(2)	5685(2)	3438(1)	13(1)
C(25)	1523(2)	6587(2)	3266(1)	14(1)
C(26)	928(2)	7050(2)	3002(1)	15(1)
C(27)	-8(2)	6630(2)	2900(1)	16(1)
C(28)	-327(2)	5736(2)	3065(1)	16(1)
C(29)	272(2)	5270(2)	3326(1)	15(1)
C(30)	1293(3)	8018(3)	2834(1)	21(1)
C(31)	-1364(3)	5329(3)	2971(1)	22(1)
C(32)	2557(2)	5910(2)	3992(1)	14(1)
C(33)	3493(2)	5669(2)	4157(1)	16(1)
C(34)	3970(3)	6316(2)	4400(1)	19(1)
C(35)	3507(3)	7234(3)	4498(1)	24(1)
C(36)	2576(3)	7484(3)	4345(1)	24(1)
C(37)	2115(3)	6832(2)	4096(1)	20(1)
C(38)	4987(3)	6038(3)	4559(1)	25(1)
C(39)	2061(4)	8471(3)	4438(1)	35(1)
C(40)	1388(2)	4288(2)	3981(1)	14(1)
C(41)	409(2)	4483(2)	4121(1)	15(1)
C(42)	-64(3)	3830(2)	4365(1)	19(1)

C(43)	435(3)	2960(2)	4486(1)	20(1)
C(44)	1410(3)	2756(2)	4353(1)	20(1)
C(45)	1869(3)	3400(2)	4105(1)	17(1)
C(46)	-1117(3)	4050(3)	4500(1)	23(1)
C(47)	1975(3)	1829(3)	4484(1)	30(1)
C(48)	2795(2)	4522(2)	3456(1)	13(1)
C(49)	2491(2)	3644(2)	3268(1)	15(1)
C(50)	3122(3)	3168(2)	3020(1)	17(1)
C(51)	4108(2)	3539(3)	2954(1)	18(1)
C(52)	4424(2)	4408(3)	3132(1)	18(1)
C(53)	3776(2)	4899(2)	3374(1)	15(1)
C(54)	2743(3)	2240(3)	2830(1)	22(1)
C(55)	5462(3)	4839(3)	3060(1)	28(1)
B(1)	1983(3)	5106(3)	3720(1)	14(1)
C(62)	64(4)	6935(4)	6353(1)	48(1)
C(63)	438(4)	7099(4)	6687(1)	50(1)
C(64)	0(5)	6572(5)	6966(1)	75(2)
C(65)	-818(4)	5924(5)	6912(1)	64(2)
C(66)	-1191(3)	5795(4)	6580(1)	49(1)
C(67)	-746(4)	6287(4)	6300(1)	50(1)
C(56)	4798(3)	3857(3)	6185(1)	39(1)
C(57)	3999(3)	3196(3)	6246(1)	40(1)
C(58)	3766(3)	2897(3)	6590(1)	42(1)
C(59)	4335(4)	3275(3)	6869(1)	44(1)
C(60)	5132(3)	3953(3)	6807(1)	40(1)
C(61)	5367(3)	4229(3)	6465(1)	39(1)

Table S–3. Bond lengths [Å] and angles [°] for crystal01.

Ni(1)-N(1)	1.892(3)	F(7)-C(38)	1.334(4)
Ni(1)-N(2)	1.898(2)	F(8)-C(38)	1.322(4)
Ni(1)-N(3)	1.896(3)	F(9)-C(38)	1.329(4)
Ni(1)-C(18)	1.881(3)	F(10)-C(39)	1.340(9)
O(1)-C(2)	1.474(4)	F(10A)-C(39)	1.460(18)
O(1)-C(3)	1.326(4)	F(10B)-C(39)	1.289(18)
O(2)-C(9)	1.326(4)	F(11)-C(39)	1.440(17)
O(2)-C(10)	1.466(4)	F(11A)-C(39)	1.206(19)
N(1)-C(1)	1.473(4)	F(11B)-C(39)	1.447(14)
N(1)-C(3)	1.290(4)	F(12)-C(39)	1.274(14)
N(2)-C(4)	1.333(4)	F(12A)-C(39)	1.285(14)
N(2)-C(8)	1.328(4)	F(12B)-C(39)	1.323(9)
N(3)-C(9)	1.285(4)	F(13)-C(46)	1.339(4)
N(3)-C(11)	1.474(4)	F(14)-C(46)	1.344(4)
C(1)-C(2)	1.544(4)	F(15)-C(46)	1.342(4)
C(1)-C(12)	1.534(5)	F(16)-C(47)	1.327(4)
C(3)-C(4)	1.470(5)	F(17)-C(47)	1.326(5)
C(4)-C(5)	1.388(4)	F(18)-C(47)	1.332(4)
C(5)-C(6)	1.387(5)	F(19)-C(54)	1.339(4)
C(6)-C(7)	1.387(5)	F(20)-C(54)	1.339(4)
C(7)-C(8)	1.387(4)	F(21)-C(54)	1.325(4)
C(8)-C(9)	1.475(4)	F(22)-C(55)	1.335(4)
C(10)-C(11)	1.548(5)	F(23)-C(55)	1.335(4)
C(11)-C(15)	1.524(5)	F(24)-C(55)	1.332(4)
C(12)-C(13)	1.521(5)	C(24)-C(25)	1.402(4)
C(12)-C(14)	1.523(5)	C(24)-C(29)	1.404(4)
C(15)-C(16)	1.521(5)	C(24)-B(1)	1.640(4)
C(15)-C(17)	1.521(5)	C(25)-C(26)	1.394(4)
C(18)-C(19)	1.394(5)	C(26)-C(27)	1.388(4)
C(18)-C(23)	1.387(5)	C(26)-C(30)	1.489(4)
C(19)-C(20)	1.384(5)	C(27)-C(28)	1.385(4)
C(20)-C(21)	1.370(6)	C(28)-C(29)	1.390(4)
C(21)-C(22)	1.373(6)	C(28)-C(31)	1.493(5)
C(22)-C(23)	1.397(5)	C(32)-C(33)	1.402(4)
F(1)-C(30)	1.339(4)	C(32)-C(37)	1.391(4)
F(2)-C(30)	1.347(4)	C(32)-B(1)	1.642(4)
F(3)-C(30)	1.342(4)	C(33)-C(34)	1.388(4)
F(4)-C(31)	1.344(4)	C(34)-C(35)	1.390(5)
F(5)-C(31)	1.342(4)	C(34)-C(38)	1.496(5)
F(6)-C(31)	1.326(4)	C(35)-C(36)	1.380(5)

C(36)-C(37)	1.396(5)	C(9)-O(2)-C(10)	105.0(2)
C(36)-C(39)	1.494(5)	C(1)-N(1)-Ni(1)	137.6(2)
C(40)-C(41)	1.401(4)	C(3)-N(1)-Ni(1)	114.1(2)
C(40)-C(45)	1.397(4)	C(3)-N(1)-C(1)	108.2(3)
C(40)-B(1)	1.642(4)	C(4)-N(2)-Ni(1)	118.8(2)
C(41)-C(42)	1.392(4)	C(8)-N(2)-Ni(1)	119.2(2)
C(42)-C(43)	1.385(4)	C(8)-N(2)-C(4)	121.9(3)
C(42)-C(46)	1.489(5)	C(9)-N(3)-Ni(1)	114.2(2)
C(43)-C(44)	1.390(5)	C(9)-N(3)-C(11)	108.3(3)
C(44)-C(45)	1.389(4)	C(11)-N(3)-Ni(1)	137.5(2)
C(44)-C(47)	1.497(5)	N(1)-C(1)-C(2)	101.7(3)
C(48)-C(49)	1.401(4)	N(1)-C(1)-C(12)	110.5(3)
C(48)-C(53)	1.402(4)	C(12)-C(1)-C(2)	115.2(3)
C(48)-B(1)	1.637(4)	O(1)-C(2)-C(1)	104.9(3)
C(49)-C(50)	1.388(4)	O(1)-C(3)-C(4)	123.3(3)
C(50)-C(51)	1.392(5)	N(1)-C(3)-O(1)	118.4(3)
C(50)-C(54)	1.490(4)	N(1)-C(3)-C(4)	118.4(3)
C(51)-C(52)	1.380(5)	N(2)-C(4)-C(3)	107.0(3)
C(52)-C(53)	1.394(4)	N(2)-C(4)-C(5)	120.8(3)
C(52)-C(55)	1.488(5)	C(5)-C(4)-C(3)	132.2(3)
C(62)-C(63)	1.359(6)	C(6)-C(5)-C(4)	117.5(3)
C(62)-C(67)	1.366(7)	C(5)-C(6)-C(7)	121.4(3)
C(63)-C(64)	1.376(7)	C(6)-C(7)-C(8)	117.3(3)
C(64)-C(65)	1.375(8)	N(2)-C(8)-C(7)	121.1(3)
C(65)-C(66)	1.345(7)	N(2)-C(8)-C(9)	106.8(3)
C(66)-C(67)	1.360(6)	C(7)-C(8)-C(9)	132.1(3)
C(56)-C(57)	1.370(6)	O(2)-C(9)-C(8)	122.8(3)
C(56)-C(61)	1.371(6)	N(3)-C(9)-O(2)	118.8(3)
C(57)-C(58)	1.382(6)	N(3)-C(9)-C(8)	118.4(3)
C(58)-C(59)	1.373(6)	O(2)-C(10)-C(11)	105.4(3)
C(59)-C(60)	1.383(6)	N(3)-C(11)-C(10)	101.7(2)
C(60)-C(61)	1.368(6)	N(3)-C(11)-C(15)	111.9(3)
		C(15)-C(11)-C(10)	115.9(3)
N(1)-Ni(1)-N(2)	81.60(11)	C(13)-C(12)-C(1)	113.0(3)
N(1)-Ni(1)-N(3)	162.99(11)	C(13)-C(12)-C(14)	111.9(3)
N(3)-Ni(1)-N(2)	81.39(11)	C(14)-C(12)-C(1)	110.1(3)
C(18)-Ni(1)-N(1)	98.22(12)	C(16)-C(15)-C(11)	110.8(3)
C(18)-Ni(1)-N(2)	179.40(13)	C(16)-C(15)-C(17)	111.6(3)
C(18)-Ni(1)-N(3)	98.78(12)	C(17)-C(15)-C(11)	112.6(3)
C(3)-O(1)-C(2)	104.9(2)	C(19)-C(18)-Ni(1)	120.6(2)

C(23)-C(18)-Ni(1)	121.5(3)	C(35)-C(36)-C(39)	120.0(3)
C(23)-C(18)-C(19)	117.9(3)	C(37)-C(36)-C(39)	119.2(3)
C(20)-C(19)-C(18)	121.1(3)	C(32)-C(37)-C(36)	122.5(3)
C(21)-C(20)-C(19)	120.2(4)	F(7)-C(38)-C(34)	112.2(3)
C(20)-C(21)-C(22)	120.1(3)	F(8)-C(38)-F(7)	106.2(3)
C(21)-C(22)-C(23)	119.9(4)	F(8)-C(38)-F(9)	106.6(3)
C(18)-C(23)-C(22)	120.8(3)	F(8)-C(38)-C(34)	113.3(3)
C(25)-C(24)-C(29)	115.9(3)	F(9)-C(38)-F(7)	105.3(3)
C(25)-C(24)-B(1)	120.5(3)	F(9)-C(38)-C(34)	112.6(3)
C(29)-C(24)-B(1)	123.2(3)	F(10)-C(39)-F(11)	103.1(7)
C(26)-C(25)-C(24)	122.1(3)	F(10)-C(39)-C(36)	113.4(5)
C(25)-C(26)-C(30)	119.3(3)	F(10A)-C(39)-C(36)	104.4(7)
C(27)-C(26)-C(25)	120.7(3)	F(10B)-C(39)-F(11B)	100.3(9)
C(27)-C(26)-C(30)	119.9(3)	F(10B)-C(39)-F(12B)	113.0(7)
C(28)-C(27)-C(26)	118.2(3)	F(10B)-C(39)-C(36)	112.3(8)
C(27)-C(28)-C(29)	121.0(3)	F(11)-C(39)-C(36)	109.8(7)
C(27)-C(28)-C(31)	117.7(3)	F(11A)-C(39)-F(10A)	105.8(12)
C(29)-C(28)-C(31)	121.2(3)	F(11A)-C(39)-F(12A)	115.1(11)
C(28)-C(29)-C(24)	122.1(3)	F(11A)-C(39)-C(36)	117.4(8)
F(1)-C(30)-F(2)	106.2(3)	F(11B)-C(39)-C(36)	112.6(6)
F(1)-C(30)-F(3)	106.2(3)	F(12)-C(39)-F(10)	112.0(7)
F(1)-C(30)-C(26)	112.5(3)	F(12)-C(39)-F(11)	104.2(8)
F(2)-C(30)-C(26)	112.5(3)	F(12)-C(39)-C(36)	113.5(7)
F(3)-C(30)-F(2)	106.4(3)	F(12A)-C(39)-F(10A)	103.7(10)
F(3)-C(30)-C(26)	112.5(3)	F(12A)-C(39)-C(36)	108.9(7)
F(4)-C(31)-C(28)	111.3(3)	F(12B)-C(39)-F(11B)	100.6(6)
F(5)-C(31)-F(4)	104.7(3)	F(12B)-C(39)-C(36)	116.3(5)
F(5)-C(31)-C(28)	112.7(3)	C(41)-C(40)-B(1)	122.3(3)
F(6)-C(31)-F(4)	107.7(3)	C(45)-C(40)-C(41)	115.6(3)
F(6)-C(31)-F(5)	106.4(3)	C(45)-C(40)-B(1)	121.8(3)
F(6)-C(31)-C(28)	113.5(3)	C(42)-C(41)-C(40)	122.5(3)
C(33)-C(32)-B(1)	121.7(3)	C(41)-C(42)-C(46)	120.9(3)
C(37)-C(32)-C(33)	115.4(3)	C(43)-C(42)-C(41)	120.7(3)
C(37)-C(32)-B(1)	122.7(3)	C(43)-C(42)-C(46)	118.5(3)
C(34)-C(33)-C(32)	122.8(3)	C(42)-C(43)-C(44)	117.9(3)
C(33)-C(34)-C(35)	120.3(3)	C(43)-C(44)-C(47)	119.0(3)
C(33)-C(34)-C(38)	120.6(3)	C(45)-C(44)-C(43)	121.1(3)
C(35)-C(34)-C(38)	119.1(3)	C(45)-C(44)-C(47)	119.9(3)
C(36)-C(35)-C(34)	118.3(3)	C(44)-C(45)-C(40)	122.2(3)
C(35)-C(36)-C(37)	120.7(3)	F(13)-C(46)-F(14)	105.9(3)

F(13)-C(46)-F(15)	106.4(3)	F(21)-C(54)-F(20)	106.2(3)
F(13)-C(46)-C(42)	113.0(3)	F(21)-C(54)-C(50)	113.0(3)
F(14)-C(46)-C(42)	112.3(3)	F(22)-C(55)-F(23)	105.8(3)
F(15)-C(46)-F(14)	105.6(3)	F(22)-C(55)-C(52)	112.8(3)
F(15)-C(46)-C(42)	113.0(3)	F(23)-C(55)-C(52)	112.1(3)
F(16)-C(47)-F(18)	106.6(3)	F(24)-C(55)-F(22)	106.6(3)
F(16)-C(47)-C(44)	112.5(3)	F(24)-C(55)-F(23)	106.2(3)
F(17)-C(47)-F(16)	106.5(3)	F(24)-C(55)-C(52)	112.8(3)
F(17)-C(47)-F(18)	106.2(3)	C(24)-B(1)-C(32)	112.5(2)
F(17)-C(47)-C(44)	111.8(3)	C(24)-B(1)-C(40)	113.3(3)
F(18)-C(47)-C(44)	112.8(3)	C(40)-B(1)-C(32)	105.1(2)
C(49)-C(48)-C(53)	115.8(3)	C(48)-B(1)-C(24)	102.6(2)
C(49)-C(48)-B(1)	120.2(3)	C(48)-B(1)-C(32)	112.4(3)
C(53)-C(48)-B(1)	123.8(3)	C(48)-B(1)-C(40)	111.2(3)
C(50)-C(49)-C(48)	122.4(3)	C(63)-C(62)-C(67)	120.5(4)
C(49)-C(50)-C(51)	120.6(3)	C(62)-C(63)-C(64)	118.2(5)
C(49)-C(50)-C(54)	119.2(3)	C(65)-C(64)-C(63)	121.1(5)
C(51)-C(50)-C(54)	120.2(3)	C(66)-C(65)-C(64)	119.5(5)
C(52)-C(51)-C(50)	118.3(3)	C(65)-C(66)-C(67)	120.1(5)
C(51)-C(52)-C(53)	120.8(3)	C(66)-C(67)-C(62)	120.6(4)
C(51)-C(52)-C(55)	119.6(3)	C(57)-C(56)-C(61)	120.3(4)
C(53)-C(52)-C(55)	119.6(3)	C(56)-C(57)-C(58)	120.0(4)
C(52)-C(53)-C(48)	122.1(3)	C(59)-C(58)-C(57)	119.4(4)
F(19)-C(54)-C(50)	111.5(3)	C(58)-C(59)-C(60)	120.4(4)
F(20)-C(54)-F(19)	105.4(3)	C(61)-C(60)-C(59)	119.6(4)
F(20)-C(54)-C(50)	112.9(3)	C(60)-C(61)-C(56)	120.2(4)
F(21)-C(54)-F(19)	107.4(3)		

Table S–4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal01. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	19(1)	17(1)	13(1)	0(1)	1(1)	-5(1)
O(1)	27(1)	29(1)	22(1)	-1(1)	5(1)	-15(1)
O(2)	23(1)	24(1)	21(1)	0(1)	-3(1)	-9(1)
N(1)	21(2)	20(1)	15(1)	-1(1)	2(1)	-3(1)
N(2)	20(1)	15(1)	16(1)	-2(1)	3(1)	-2(1)
N(3)	21(2)	18(1)	15(1)	-1(1)	0(1)	-3(1)
C(1)	22(2)	23(2)	21(2)	-2(1)	2(1)	-11(2)
C(2)	21(2)	32(2)	23(2)	-4(2)	5(1)	-9(2)
C(3)	25(2)	19(2)	19(2)	-1(1)	6(1)	-5(1)
C(4)	27(2)	20(2)	15(2)	-1(1)	3(1)	-6(2)
C(5)	36(2)	26(2)	17(2)	2(1)	5(2)	-6(2)
C(6)	39(2)	30(2)	12(2)	0(1)	1(1)	-2(2)
C(7)	30(2)	21(2)	18(2)	-3(1)	-4(2)	-2(2)
C(8)	22(2)	14(2)	18(2)	-1(1)	-2(1)	-2(1)
C(9)	19(2)	14(2)	19(2)	-2(1)	-1(1)	2(1)
C(10)	24(2)	23(2)	23(2)	2(1)	3(1)	-8(2)
C(11)	22(2)	20(2)	18(2)	1(1)	1(1)	-10(1)
C(12)	31(2)	27(2)	23(2)	-6(2)	10(2)	-14(2)
C(13)	34(2)	33(2)	41(2)	-11(2)	1(2)	-4(2)
C(14)	54(3)	40(2)	25(2)	-8(2)	5(2)	-21(2)
C(15)	36(2)	26(2)	22(2)	7(1)	-7(2)	-16(2)
C(16)	71(3)	31(2)	23(2)	1(2)	4(2)	-22(2)
C(17)	31(2)	30(2)	40(2)	12(2)	1(2)	-2(2)
C(18)	23(2)	17(1)	16(1)	-1(1)	0(1)	-10(2)
C(19)	30(2)	26(2)	22(2)	-1(1)	-2(2)	-7(2)
C(20)	44(2)	37(2)	29(2)	5(2)	-14(2)	-8(2)
C(21)	52(3)	47(3)	14(2)	0(2)	-4(2)	-21(2)
C(22)	42(2)	38(2)	20(2)	-6(2)	10(2)	-13(2)
C(23)	26(2)	28(2)	22(2)	-1(1)	2(1)	-7(2)
F(1)	40(1)	19(1)	29(1)	3(1)	-7(1)	-9(1)
F(2)	36(1)	26(1)	34(1)	17(1)	-12(1)	-6(1)
F(3)	34(1)	35(1)	33(1)	9(1)	14(1)	-6(1)
F(4)	15(1)	63(2)	40(1)	-18(1)	2(1)	0(1)
F(5)	25(1)	31(1)	23(1)	-5(1)	-9(1)	-1(1)

F(6)	38(1)	43(1)	65(2)	34(1)	-28(1)	-25(1)
F(7)	29(1)	65(2)	58(2)	-29(1)	-18(1)	17(1)
F(8)	37(1)	81(2)	44(1)	31(1)	-18(1)	-6(1)
F(9)	34(1)	35(1)	70(2)	-3(1)	-26(1)	-9(1)
F(10)	44(5)	34(3)	44(5)	-30(3)	-14(3)	17(3)
F(10A)	42(5)	30(3)	47(5)	-22(4)	-2(4)	14(3)
F(10B)	48(5)	27(3)	49(5)	-3(3)	0(3)	16(4)
F(11)	35(6)	23(3)	40(5)	-3(3)	-16(3)	9(4)
F(11A)	41(5)	36(3)	46(5)	-12(3)	-6(3)	18(3)
F(11B)	35(4)	43(3)	45(5)	-20(3)	-7(3)	18(3)
F(12)	41(5)	47(3)	46(5)	-18(4)	7(3)	19(3)
F(12A)	42(5)	43(3)	46(5)	-25(3)	1(3)	16(3)
F(12B)	39(4)	41(3)	44(4)	-35(3)	-12(3)	16(3)
F(13)	38(1)	46(1)	36(1)	-19(1)	19(1)	-6(1)
F(14)	29(1)	28(1)	38(1)	2(1)	12(1)	-8(1)
F(15)	24(1)	44(1)	51(1)	22(1)	14(1)	11(1)
F(16)	59(2)	35(1)	55(2)	21(1)	24(1)	28(1)
F(17)	90(2)	54(2)	65(2)	12(1)	-48(2)	22(2)
F(18)	51(2)	31(1)	68(2)	31(1)	22(1)	13(1)
F(19)	43(1)	28(1)	38(1)	-6(1)	-25(1)	-3(1)
F(20)	43(1)	17(1)	42(1)	1(1)	-14(1)	-3(1)
F(21)	57(2)	56(2)	59(2)	-45(1)	33(1)	-22(1)
F(22)	22(1)	60(2)	31(1)	-10(1)	0(1)	-17(1)
F(23)	39(1)	82(2)	45(1)	31(1)	-4(1)	-32(1)
F(24)	19(1)	70(2)	89(2)	-36(2)	21(1)	-5(1)
C(24)	13(2)	16(2)	11(1)	-2(1)	3(1)	4(1)
C(25)	14(2)	15(2)	15(2)	-1(1)	2(1)	-1(1)
C(26)	19(2)	12(1)	14(1)	0(1)	4(1)	0(1)
C(27)	18(2)	17(2)	12(1)	1(1)	-3(1)	3(1)
C(28)	15(2)	16(2)	15(2)	0(1)	-1(1)	-1(1)
C(29)	17(2)	15(2)	13(1)	0(1)	-1(1)	2(1)
C(30)	23(2)	19(2)	21(2)	5(1)	-1(1)	-2(1)
C(31)	21(2)	21(2)	24(2)	5(1)	-4(1)	-1(1)
C(32)	16(2)	15(2)	11(1)	0(1)	0(1)	0(1)
C(33)	20(2)	13(2)	16(2)	-1(1)	0(1)	1(1)
C(34)	22(2)	19(2)	17(2)	1(1)	-7(1)	-2(1)
C(35)	32(2)	21(2)	18(2)	-6(1)	-8(2)	0(2)
C(36)	34(2)	19(2)	19(2)	-6(1)	-2(2)	4(2)
C(37)	23(2)	20(2)	16(2)	-1(1)	-5(1)	3(1)
C(38)	24(2)	27(2)	23(2)	-3(1)	-7(2)	-3(2)

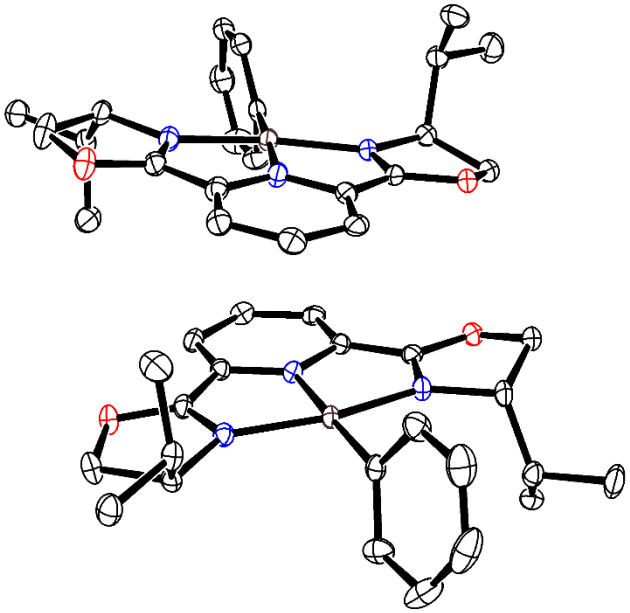
C(39)	47(3)	28(2)	31(2)	-14(2)	-11(2)	9(2)
C(40)	17(2)	13(2)	12(1)	-1(1)	-1(1)	0(1)
C(41)	18(2)	15(2)	12(1)	-1(1)	-1(1)	4(1)
C(42)	21(2)	20(2)	16(2)	-1(1)	3(1)	1(1)
C(43)	27(2)	17(2)	15(2)	4(1)	3(1)	-2(1)
C(44)	29(2)	17(2)	15(2)	3(1)	-4(1)	2(1)
C(45)	18(2)	20(2)	13(1)	1(1)	0(1)	3(1)
C(46)	25(2)	20(2)	25(2)	2(1)	6(2)	-2(2)
C(47)	35(2)	27(2)	28(2)	12(2)	4(2)	8(2)
C(48)	12(2)	14(2)	13(1)	1(1)	-2(1)	3(1)
C(49)	14(2)	17(2)	14(1)	2(1)	-1(1)	1(1)
C(50)	21(2)	16(2)	15(1)	-2(1)	-3(1)	1(1)
C(51)	18(2)	24(2)	13(1)	-1(1)	3(1)	3(1)
C(52)	15(2)	22(2)	17(2)	4(1)	1(1)	0(1)
C(53)	15(2)	18(2)	13(1)	0(1)	-2(1)	-1(1)
C(54)	22(2)	25(2)	20(2)	-7(1)	3(1)	0(2)
C(55)	19(2)	41(2)	24(2)	-1(2)	4(1)	-5(2)
B(1)	15(2)	14(2)	13(1)	1(1)	-3(1)	2(2)
C(62)	48(3)	55(3)	41(2)	19(2)	8(2)	5(2)
C(63)	45(3)	52(3)	53(3)	-16(2)	5(2)	1(2)
C(64)	66(4)	134(6)	24(2)	-11(3)	2(2)	16(4)
C(65)	58(3)	86(4)	46(3)	31(3)	23(3)	14(3)
C(66)	34(2)	45(3)	68(3)	0(2)	13(2)	9(2)
C(67)	43(3)	76(4)	33(2)	4(2)	-7(2)	8(3)
C(56)	48(3)	38(2)	32(2)	-1(2)	6(2)	16(2)
C(57)	51(3)	28(2)	41(2)	-10(2)	-13(2)	11(2)
C(58)	41(3)	28(2)	55(3)	7(2)	-10(2)	5(2)
C(59)	51(3)	52(3)	31(2)	16(2)	-5(2)	15(2)
C(60)	41(3)	42(2)	38(2)	-9(2)	-17(2)	10(2)
C(61)	31(2)	30(2)	56(3)	-1(2)	1(2)	8(2)

Table S–5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for crystal01.

	x	y	z	U(eq)
H(1)	-228	3968	5865	26
H(2A)	-1258	3478	6312	31
H(2B)	-741	2360	6285	31
H(5)	1004	3795	7339	31
H(6)	2303	4689	7641	33
H(7)	3460	5731	7326	28
H(10A)	5302	6556	6245	28
H(10B)	4701	7630	6278	28
H(11)	4177	6051	5834	24
H(12)	1269	3007	5681	32
H(13A)	1607	2173	6234	54
H(13B)	1620	1400	5902	54
H(13C)	645	1437	6162	54
H(14A)	348	1711	5392	59
H(14B)	-303	2751	5388	59
H(14C)	-593	1856	5662	59
H(15)	2671	7000	5680	33
H(16A)	4504	8194	5658	62
H(16B)	3530	8363	5404	62
H(16C)	4197	7337	5372	62
H(17A)	2371	7762	6250	51
H(17B)	2291	8564	5928	51
H(17C)	3297	8537	6173	51
H(19)	566	5830	5638	31
H(20)	479	5939	5019	44
H(21)	1755	5213	4670	45
H(22)	3132	4377	4936	40
H(23)	3245	4287	5559	30
H(25)	2159	6892	3331	17
H(27)	-418	6948	2722	19
H(29)	37	4651	3432	18
H(33)	3815	5037	4100	19
H(35)	3823	7677	4666	28
H(37)	1474	7026	3995	24
H(41)	55	5083	4048	18

H(43)	121	2518	4655	23
H(45)	2533	3232	4017	20
H(49)	1830	3364	3313	18
H(51)	4551	3201	2790	22
H(53)	4006	5509	3487	18
H(62)	367	7275	6155	58
H(63)	988	7565	6726	60
H(64)	268	6657	7200	90
H(65)	-1119	5570	7107	76
H(66)	-1765	5360	6542	59
H(67)	-1000	6177	6066	61
H(56)	4958	4059	5948	47
H(57)	3606	2942	6051	48
H(58)	3215	2436	6634	50
H(59)	4182	3068	7107	53
H(60)	5514	4226	7001	48
H(61)	5925	4680	6420	47

((–)-*i*-Pr-pybox)Ni^{II}Ph (2). A suitable crystal of $C_{23}H_{28}N_3NiO_2$ was selected for analysis, mounted in a nylon loop and frozen in liquid nitrogen. All measurements were made at the SSRL synchrotron with 0.72930 Å radiation at a temperature of 100 K. Using Olex2,[5] the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL[6] refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the known stereochemistry of the commercially available ligand and the absolute structure parameter.



ORTEP diagram of the asymmetric unit with ellipsoids shown at 30% probability

Table S–6. Crystal data and structure refinement for crystal02.

Identification code	((–)-*i*-Pr-pybox)NiPh	
Empirical formula	$C_{23}H_{28}N_3NiO_2$	
Formula weight	437.19	
Temperature	100 K	
Wavelength	0.72930 Å (synchrotron)	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.450(2) Å	α= 90°.
	b = 11.491(2) Å	β= 99.75(3)°.
	c = 18.143(4) Å	γ = 90°.
Volume	2147.2(7) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	0.927 mm^{-1}	
F(000)	924	
Crystal size	0.11 x 0.06 x 0.02 mm^3	
Theta range for data collection	1.17 to 31.38°.	
Index ranges	-13<=h<=14, -16<=k<=14, -17<=l<=24	
Reflections collected	18095	
Independent reflections	9894 [R(int) = 0.0423]	
Completeness to theta = 26.50°	95.8 %	
Absorption correction	Semi-empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9894 / 1 / 531	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.1013	
R indices (all data)	R1 = 0.0446, wR2 = 0.1031	
Absolute structure parameter	0.048(9)	
Largest diff. peak and hole	0.844 and -0.487 $e/Å^{-3}$	

Table S–7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for crystal02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	-6599(2)	-8732(2)	-1048(1)	34(1)
O(2)	-2446(2)	-5412(2)	-2924(1)	42(1)
O(3)	-3367(2)	-8340(2)	-4731(1)	32(1)
O(4)	-6500(2)	-10800(2)	-1928(1)	31(1)
N(1)	-4516(2)	-8103(2)	-802(1)	30(1)
N(2)	-4513(2)	-7098(2)	-2004(1)	32(1)
N(3)	-2287(2)	-6298(2)	-1796(2)	32(1)
N(4)	-5399(2)	-8934(2)	-4643(1)	26(1)
N(5)	-4906(2)	-9505(2)	-3311(1)	26(1)
N(6)	-7027(2)	-10278(2)	-3145(1)	27(1)
C(1)	-4710(3)	-8686(3)	-109(2)	34(1)
C(2)	-6009(3)	-9319(3)	-362(2)	38(1)
C(3)	-5608(3)	-8175(2)	-1284(2)	29(1)
C(4)	-5680(3)	-7643(3)	-1994(2)	31(1)
C(5)	-6650(3)	-7594(3)	-2627(2)	33(1)
C(6)	-6395(3)	-7034(3)	-3264(2)	37(1)
C(7)	-5186(3)	-6499(3)	-3273(2)	34(1)
C(8)	-4283(3)	-6561(3)	-2629(2)	33(1)
C(9)	-2961(3)	-6088(3)	-2449(2)	34(1)
C(10)	-1174(3)	-5071(3)	-2519(2)	50(1)
C(11)	-1050(3)	-5633(3)	-1741(2)	37(1)
C(12)	-4764(3)	-7823(3)	530(2)	41(1)
C(13)	-4836(5)	-8490(4)	1257(2)	63(1)
C(14)	-5854(4)	-6936(4)	342(2)	57(1)
C(15)	182(3)	-6353(3)	-1507(2)	36(1)
C(16)	1393(3)	-5582(3)	-1489(2)	49(1)
C(17)	225(3)	-7420(3)	-1998(2)	48(1)
C(18)	-1821(3)	-7414(3)	-350(2)	33(1)
C(19)	-1374(3)	-6527(3)	158(2)	37(1)
C(20)	-234(3)	-6621(3)	679(2)	42(1)
C(21)	509(4)	-7629(4)	703(2)	49(1)
C(22)	85(4)	-8522(3)	215(2)	54(1)
C(23)	-1063(4)	-8430(3)	-283(2)	43(1)
C(24)	-5486(3)	-8665(2)	-5451(2)	27(1)

C(25)	-4065(3)	-8276(3)	-5489(2)	37(1)
C(26)	-4217(3)	-8737(2)	-4313(2)	26(1)
C(27)	-3850(3)	-9044(2)	-3532(2)	26(1)
C(28)	-2675(3)	-8976(2)	-3058(2)	30(1)
C(29)	-2605(3)	-9403(2)	-2322(2)	31(1)
C(30)	-3698(3)	-9877(2)	-2094(2)	28(1)
C(31)	-4865(3)	-9915(2)	-2594(2)	26(1)
C(32)	-6136(3)	-10328(2)	-2546(2)	26(1)
C(33)	-7905(3)	-10804(3)	-2090(2)	34(1)
C(34)	-8244(3)	-10759(3)	-2955(2)	31(1)
C(35)	-6519(3)	-7773(3)	-5760(2)	30(1)
C(36)	-6469(3)	-7563(3)	-6591(2)	38(1)
C(37)	-6400(4)	-6646(3)	-5327(2)	47(1)
C(38)	-8604(3)	-11932(3)	-3338(2)	33(1)
C(39)	-10015(3)	-12227(4)	-3296(2)	49(1)
C(40)	-7720(3)	-12920(3)	-3009(2)	36(1)
C(41)	-8061(3)	-9770(3)	-4656(2)	27(1)
C(42)	-9161(3)	-9134(3)	-4578(2)	38(1)
C(43)	-10352(3)	-9336(4)	-5008(2)	55(1)
C(44)	-10506(4)	-10209(4)	-5523(3)	61(1)
C(45)	-9441(4)	-10870(3)	-5626(2)	53(1)
C(46)	-8225(4)	-10639(3)	-5206(2)	38(1)

Table S–8. Bond lengths [Å] and angles [°] for crystal02.

Ni(1)-N(2)	1.871(3)	C(4)-C(5)	1.398(4)
Ni(1)-N(1)	1.906(2)	C(28)-C(29)	1.413(4)
Ni(1)-C(18)	1.896(3)	C(32)-C(31)	1.427(4)
Ni(1)-N(3)	1.934(3)	C(5)-C(6)	1.388(5)
Ni(2)-N(5)	1.874(2)	C(24)-C(25)	1.564(4)
Ni(2)-C(41)	1.895(3)	C(24)-C(35)	1.524(4)
Ni(2)-N(6)	1.897(2)	C(46)-C(45)	1.392(5)
Ni(2)-N(4)	1.920(2)	O(2)-C(9)	1.340(4)
C(39)-C(38)	1.527(4)	O(2)-C(10)	1.459(4)
N(5)-C(27)	1.345(3)	C(19)-C(20)	1.394(5)
N(5)-C(31)	1.377(4)	C(2)-C(1)	1.540(4)
N(2)-C(4)	1.374(4)	C(6)-C(7)	1.408(4)
N(2)-C(8)	1.348(4)	C(11)-C(10)	1.538(5)
O(4)-C(32)	1.356(3)	C(11)-C(15)	1.529(4)
O(4)-C(33)	1.448(4)	C(20)-C(21)	1.392(5)
O(1)-C(3)	1.347(3)	C(1)-C(12)	1.534(4)
O(1)-C(2)	1.457(4)	C(38)-C(40)	1.520(5)
C(41)-C(46)	1.401(4)	C(9)-C(8)	1.469(4)
C(41)-C(42)	1.390(4)	C(8)-C(7)	1.374(5)
N(6)-C(34)	1.479(3)	C(14)-C(12)	1.523(6)
N(6)-C(32)	1.307(4)	C(15)-C(17)	1.520(5)
N(4)-C(24)	1.487(4)	C(15)-C(16)	1.540(4)
N(4)-C(26)	1.298(4)	C(36)-C(35)	1.538(4)
O(3)-C(26)	1.343(3)	C(22)-C(23)	1.379(5)
O(3)-C(25)	1.446(4)	C(22)-C(21)	1.378(6)
N(1)-C(3)	1.318(4)	C(42)-C(43)	1.372(5)
N(1)-C(1)	1.469(4)	C(35)-C(37)	1.508(5)
C(18)-C(19)	1.400(5)	C(12)-C(13)	1.539(5)
C(18)-C(23)	1.405(5)	C(43)-C(44)	1.361(7)
C(27)-C(28)	1.376(4)	C(45)-C(44)	1.386(7)
C(27)-C(26)	1.448(4)		
C(34)-C(38)	1.534(4)	N(2)-Ni(1)-N(1)	81.56(11)
C(34)-C(33)	1.550(4)	N(2)-Ni(1)-C(18)	177.48(13)
C(3)-C(4)	1.416(4)	N(2)-Ni(1)-N(3)	80.90(11)
N(3)-C(11)	1.491(4)	N(1)-Ni(1)-N(3)	162.44(11)
N(3)-C(9)	1.293(4)	C(18)-Ni(1)-N(1)	99.74(12)
C(30)-C(31)	1.392(4)	C(18)-Ni(1)-N(3)	97.83(12)
C(30)-C(29)	1.390(4)	N(5)-Ni(2)-C(41)	177.39(12)

N(5)-Ni(2)-N(6)	81.19(10)	C(9)-N(3)-C(11)	107.3(3)
N(5)-Ni(2)-N(4)	81.31(10)	C(29)-C(30)-C(31)	119.4(3)
C(41)-Ni(2)-N(6)	96.67(11)	N(2)-C(4)-C(3)	107.3(3)
C(41)-Ni(2)-N(4)	100.78(11)	N(2)-C(4)-C(5)	119.6(3)
N(6)-Ni(2)-N(4)	162.42(10)	C(5)-C(4)-C(3)	133.1(3)
C(27)-N(5)-Ni(2)	119.7(2)	C(27)-C(28)-C(29)	117.9(3)
C(27)-N(5)-C(31)	121.3(2)	O(4)-C(32)-C(31)	125.3(3)
C(31)-N(5)-Ni(2)	118.98(18)	N(6)-C(32)-O(4)	116.4(3)
C(4)-N(2)-Ni(1)	118.8(2)	N(6)-C(32)-C(31)	118.3(2)
C(8)-N(2)-Ni(1)	120.7(2)	N(5)-C(31)-C(30)	119.3(2)
C(8)-N(2)-C(4)	120.3(3)	N(5)-C(31)-C(32)	106.9(2)
C(32)-O(4)-C(33)	104.5(2)	C(30)-C(31)-C(32)	133.8(3)
C(3)-O(1)-C(2)	104.8(2)	C(6)-C(5)-C(4)	119.2(3)
C(46)-C(41)-Ni(2)	120.9(2)	N(4)-C(24)-C(25)	101.7(2)
C(42)-C(41)-Ni(2)	122.4(2)	N(4)-C(24)-C(35)	115.0(2)
C(42)-C(41)-C(46)	116.3(3)	C(35)-C(24)-C(25)	114.3(2)
C(34)-N(6)-Ni(2)	137.4(2)	C(45)-C(46)-C(41)	121.1(3)
C(32)-N(6)-Ni(2)	114.58(19)	C(9)-O(2)-C(10)	105.2(3)
C(32)-N(6)-C(34)	108.0(2)	N(4)-C(26)-O(3)	117.9(3)
C(24)-N(4)-Ni(2)	138.32(19)	N(4)-C(26)-C(27)	118.9(3)
C(26)-N(4)-Ni(2)	113.1(2)	O(3)-C(26)-C(27)	123.0(3)
C(26)-N(4)-C(24)	108.3(2)	C(20)-C(19)-C(18)	122.8(3)
C(26)-O(3)-C(25)	106.2(2)	O(1)-C(2)-C(1)	105.1(2)
C(3)-N(1)-Ni(1)	113.4(2)	C(5)-C(6)-C(7)	120.7(3)
C(3)-N(1)-C(1)	108.1(2)	N(3)-C(11)-C(10)	102.5(3)
C(1)-N(1)-Ni(1)	138.5(2)	N(3)-C(11)-C(15)	114.9(3)
C(19)-C(18)-Ni(1)	124.3(3)	C(15)-C(11)-C(10)	114.7(3)
C(19)-C(18)-C(23)	115.3(3)	C(21)-C(20)-C(19)	119.6(3)
C(23)-C(18)-Ni(1)	119.9(3)	N(1)-C(1)-C(2)	101.7(3)
N(5)-C(27)-C(28)	121.8(3)	N(1)-C(1)-C(12)	112.3(3)
N(5)-C(27)-C(26)	107.0(2)	C(12)-C(1)-C(2)	112.8(3)
C(28)-C(27)-C(26)	131.2(3)	C(39)-C(38)-C(34)	109.7(3)
N(6)-C(34)-C(38)	112.2(2)	C(40)-C(38)-C(39)	110.0(3)
N(6)-C(34)-C(33)	101.0(2)	C(40)-C(38)-C(34)	113.1(2)
C(38)-C(34)-C(33)	115.3(2)	N(3)-C(9)-O(2)	118.8(3)
O(1)-C(3)-C(4)	124.7(3)	N(3)-C(9)-C(8)	118.7(3)
N(1)-C(3)-O(1)	116.4(3)	O(2)-C(9)-C(8)	122.4(3)
N(1)-C(3)-C(4)	118.9(3)	O(2)-C(10)-C(11)	106.1(3)
C(11)-N(3)-Ni(1)	139.0(2)	C(30)-C(29)-C(28)	120.3(3)
C(9)-N(3)-Ni(1)	113.4(2)	N(2)-C(8)-C(9)	106.1(3)

N(2)-C(8)-C(7)	123.0(3)	C(37)-C(35)-C(24)	113.3(3)
C(7)-C(8)-C(9)	131.0(3)	C(37)-C(35)-C(36)	111.2(3)
C(8)-C(7)-C(6)	117.2(3)	C(1)-C(12)-C(13)	109.8(3)
O(3)-C(25)-C(24)	105.9(2)	C(14)-C(12)-C(1)	112.6(3)
C(11)-C(15)-C(16)	110.1(3)	C(14)-C(12)-C(13)	112.5(3)
C(17)-C(15)-C(11)	112.4(3)	C(22)-C(23)-C(18)	122.4(3)
C(17)-C(15)-C(16)	111.8(3)	C(44)-C(43)-C(42)	120.4(4)
O(4)-C(33)-C(34)	104.8(2)	C(22)-C(21)-C(20)	118.8(4)
C(21)-C(22)-C(23)	121.0(4)	C(44)-C(45)-C(46)	120.0(4)
C(43)-C(42)-C(41)	122.6(3)	C(43)-C(44)-C(45)	119.5(3)
C(24)-C(35)-C(36)	109.0(3)		

Table S–9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for crystal02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni(1)	27(1)	28(1)	35(1)	0(1)	11(1)	-3(1)
Ni(2)	22(1)	22(1)	26(1)	4(1)	8(1)	-2(1)
O(1)	33(1)	36(1)	36(1)	-5(1)	14(1)	-9(1)
O(2)	37(1)	39(1)	50(2)	15(1)	10(1)	-4(1)
O(3)	22(1)	39(1)	34(1)	10(1)	9(1)	-1(1)
O(4)	37(1)	33(1)	25(1)	1(1)	11(1)	-6(1)
N(1)	33(1)	30(1)	30(1)	-3(1)	13(1)	-7(1)
N(2)	30(1)	30(1)	38(2)	1(1)	11(1)	-6(1)
N(3)	27(1)	30(1)	41(2)	3(1)	10(1)	-2(1)
N(4)	26(1)	23(1)	30(1)	3(1)	8(1)	1(1)
N(5)	26(1)	23(1)	28(1)	1(1)	7(1)	-4(1)
N(6)	25(1)	29(1)	28(1)	3(1)	8(1)	-4(1)
C(1)	40(2)	36(2)	29(2)	-3(1)	11(1)	-6(1)
C(2)	49(2)	37(2)	32(2)	-5(1)	17(1)	-12(1)
C(3)	25(1)	28(1)	37(2)	-7(1)	11(1)	-5(1)
C(4)	27(1)	30(1)	38(2)	-6(1)	11(1)	0(1)
C(5)	26(1)	28(1)	46(2)	-9(1)	9(1)	3(1)
C(6)	35(2)	36(2)	40(2)	1(1)	6(1)	9(1)
C(7)	36(2)	28(1)	41(2)	7(1)	10(1)	6(1)
C(8)	32(2)	25(1)	44(2)	4(1)	10(1)	2(1)
C(9)	37(2)	23(1)	43(2)	4(1)	16(1)	4(1)
C(10)	36(2)	44(2)	72(3)	21(2)	11(2)	-7(2)
C(11)	31(2)	31(2)	50(2)	-1(1)	14(1)	-6(1)
C(12)	42(2)	51(2)	33(2)	-14(2)	13(2)	-17(2)
C(13)	72(3)	85(3)	35(2)	-13(2)	18(2)	-34(2)
C(14)	52(2)	65(3)	57(3)	-32(2)	22(2)	-13(2)
C(15)	31(2)	39(2)	41(2)	0(1)	14(1)	-2(1)
C(16)	36(2)	52(2)	62(3)	-10(2)	16(2)	-12(2)
C(17)	32(2)	40(2)	75(3)	-7(2)	18(2)	2(1)
C(18)	31(2)	34(2)	37(2)	3(1)	17(1)	-4(1)
C(19)	29(2)	38(2)	46(2)	-6(1)	15(1)	-3(1)
C(20)	39(2)	48(2)	40(2)	-9(2)	15(2)	-11(2)
C(21)	48(2)	59(2)	39(2)	12(2)	7(2)	2(2)
C(22)	69(3)	46(2)	42(2)	2(2)	-2(2)	14(2)

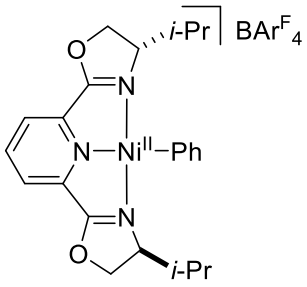
C(23)	58(2)	32(2)	37(2)	3(1)	2(2)	2(2)
C(24)	33(2)	26(1)	25(2)	3(1)	11(1)	-1(1)
C(25)	30(2)	50(2)	32(2)	11(1)	12(1)	2(1)
C(26)	25(1)	21(1)	34(2)	5(1)	11(1)	1(1)
C(27)	28(1)	22(1)	28(2)	2(1)	8(1)	1(1)
C(28)	25(1)	25(1)	40(2)	1(1)	8(1)	-2(1)
C(29)	32(1)	29(2)	32(2)	1(1)	-1(1)	1(1)
C(30)	38(2)	20(1)	26(2)	0(1)	3(1)	2(1)
C(31)	34(1)	21(1)	25(2)	2(1)	10(1)	-1(1)
C(32)	34(2)	22(1)	23(2)	-1(1)	7(1)	-3(1)
C(33)	37(2)	34(2)	35(2)	-2(1)	17(1)	-10(1)
C(34)	29(2)	34(1)	32(2)	5(1)	14(1)	-6(1)
C(35)	26(1)	31(1)	32(2)	9(1)	6(1)	-2(1)
C(36)	40(2)	40(2)	34(2)	9(1)	6(1)	-4(1)
C(37)	63(2)	34(2)	45(2)	10(2)	17(2)	16(2)
C(38)	35(2)	40(2)	24(2)	3(1)	6(1)	-13(1)
C(39)	40(2)	55(2)	56(2)	5(2)	14(2)	-24(2)
C(40)	44(2)	35(2)	32(2)	-6(1)	12(1)	-9(1)
C(41)	27(1)	28(2)	25(2)	8(1)	6(1)	-3(1)
C(42)	28(2)	46(2)	40(2)	-1(2)	6(1)	5(1)
C(43)	27(2)	75(3)	63(3)	15(2)	5(2)	3(2)
C(44)	46(2)	69(3)	56(3)	28(2)	-20(2)	-26(2)
C(45)	76(3)	32(2)	40(2)	6(2)	-17(2)	-16(2)
C(46)	53(2)	34(2)	24(2)	2(1)	1(1)	2(1)

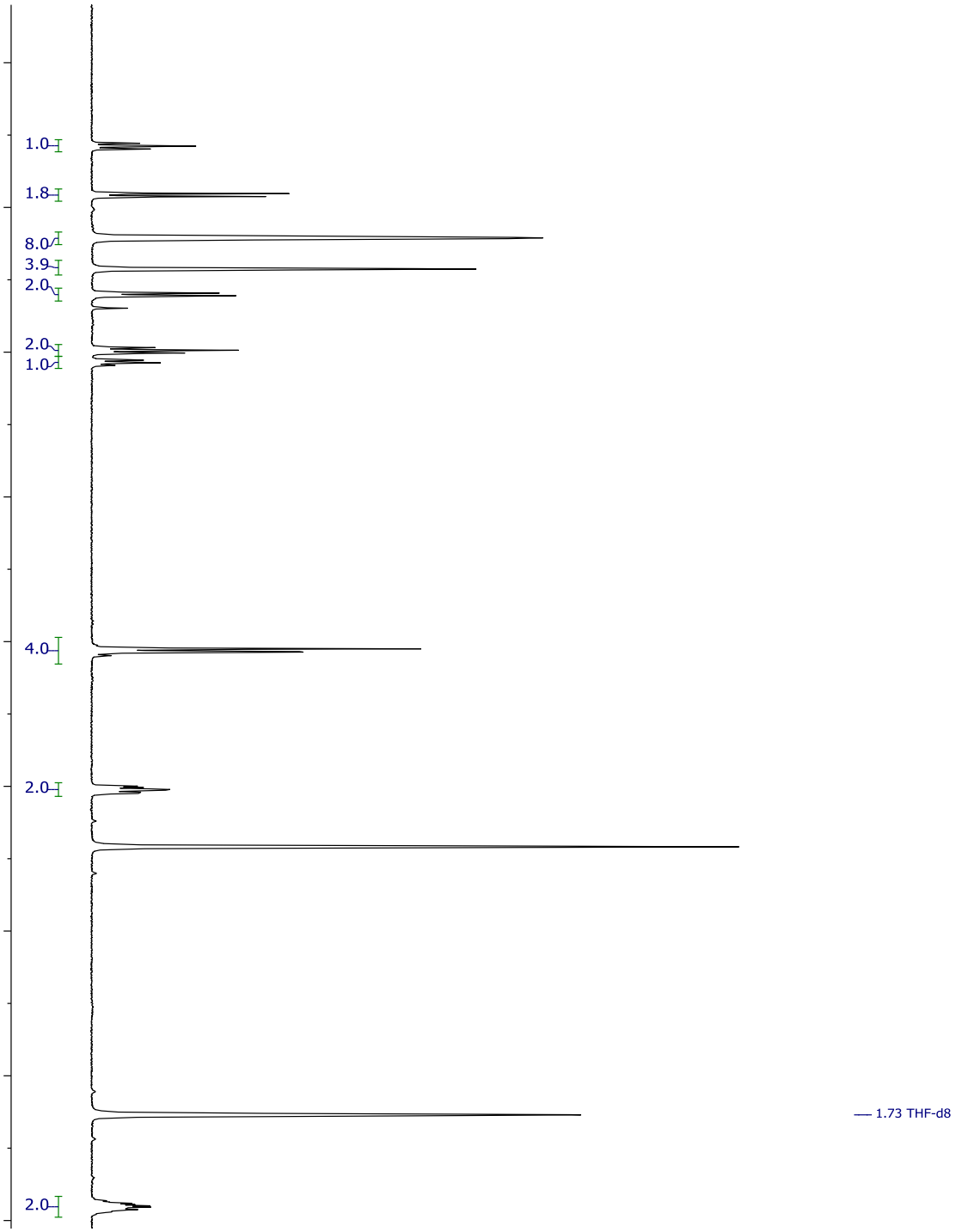
Table S–10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for crystal02.

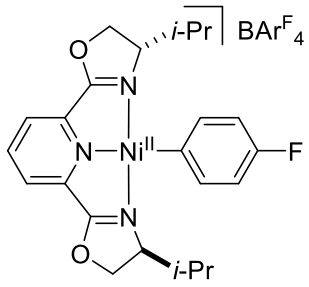
	x	y	z	U(eq)
H(1)	-4002	-9267	45	41
H(5)	-7474	-7940	-2620	40
H(6)	-7044	-7011	-3699	44
H(7)	-5003	-6112	-3706	41
H(11)	-1060	-4997	-1365	44
H(12)	-3927	-7381	611	49
H(15)	179	-6633	-985	43
H(19)	-1869	-5832	147	44
H(20)	34	-5999	1015	50
H(21)	1295	-7702	1050	59
H(22)	590	-9210	223	64
H(23)	-1352	-9077	-593	52
H(24)	-5669	-9403	-5742	33
H(28)	-1934	-8653	-3221	36
H(29)	-1808	-9367	-1982	38
H(30)	-3649	-10171	-1601	34
H(34)	-8967	-10193	-3106	37
H(35)	-7386	-8117	-5726	36
H(38)	-8526	-11852	-3878	40
H(42)	-9086	-8536	-4211	46
H(43)	-11072	-8864	-4947	66
H(44)	-11337	-10364	-5808	73
H(45)	-9541	-11482	-5984	63
H(46)	-7495	-11077	-5293	45
H(10A)	-1110	-4214	-2476	61
H(10B)	-478	-5355	-2783	61
H(13A)	-5609	-8987	1184	94
H(13B)	-4886	-7935	1661	94
H(13C)	-4058	-8974	1390	94
H(14A)	-5769	-6537	-125	85
H(14B)	-5799	-6365	747	85
H(14C)	-6694	-7335	282	85
H(16A)	1420	-5287	-1993	74
H(16B)	2175	-6043	-1315	74
H(16C)	1353	-4926	-1149	74

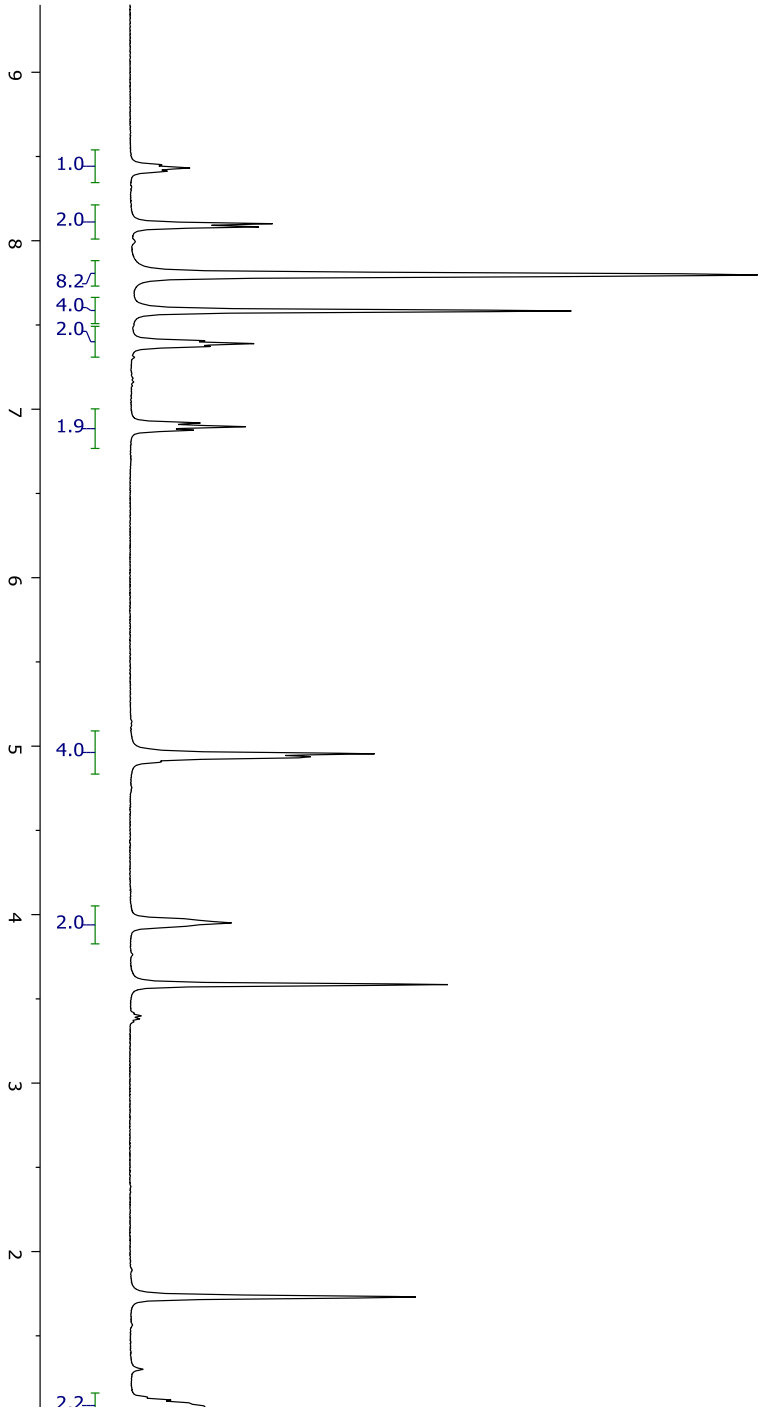
H(17A)	-584	-7861	-2022	72
H(17B)	961	-7912	-1785	72
H(17C)	324	-7174	-2502	72
H(25A)	-3668	-8800	-5820	44
H(25B)	-4053	-7471	-5683	44
H(2A)	-5862	-10152	-457	45
H(2B)	-6572	-9256	23	45
H(33A)	-8263	-10118	-1864	41
H(33B)	-8257	-11519	-1894	41
H(36A)	-5642	-7194	-6640	57
H(36B)	-7187	-7052	-6806	57
H(36C)	-6547	-8308	-6858	57
H(37A)	-6347	-6811	-4793	70
H(37B)	-7162	-6159	-5500	70
H(37C)	-5614	-6235	-5408	70
H(39A)	-10126	-12266	-2772	74
H(39B)	-10238	-12981	-3537	74
H(39C)	-10585	-11623	-3554	74
H(40A)	-7804	-13034	-2484	54
H(40B)	-6818	-12727	-3042	54
H(40C)	-7970	-13637	-3290	54

IX. ^{1}H NMR Spectra

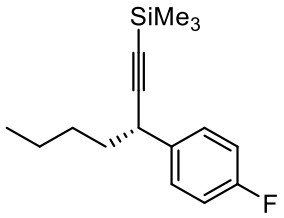








1.73 THF-d8


SiMe3
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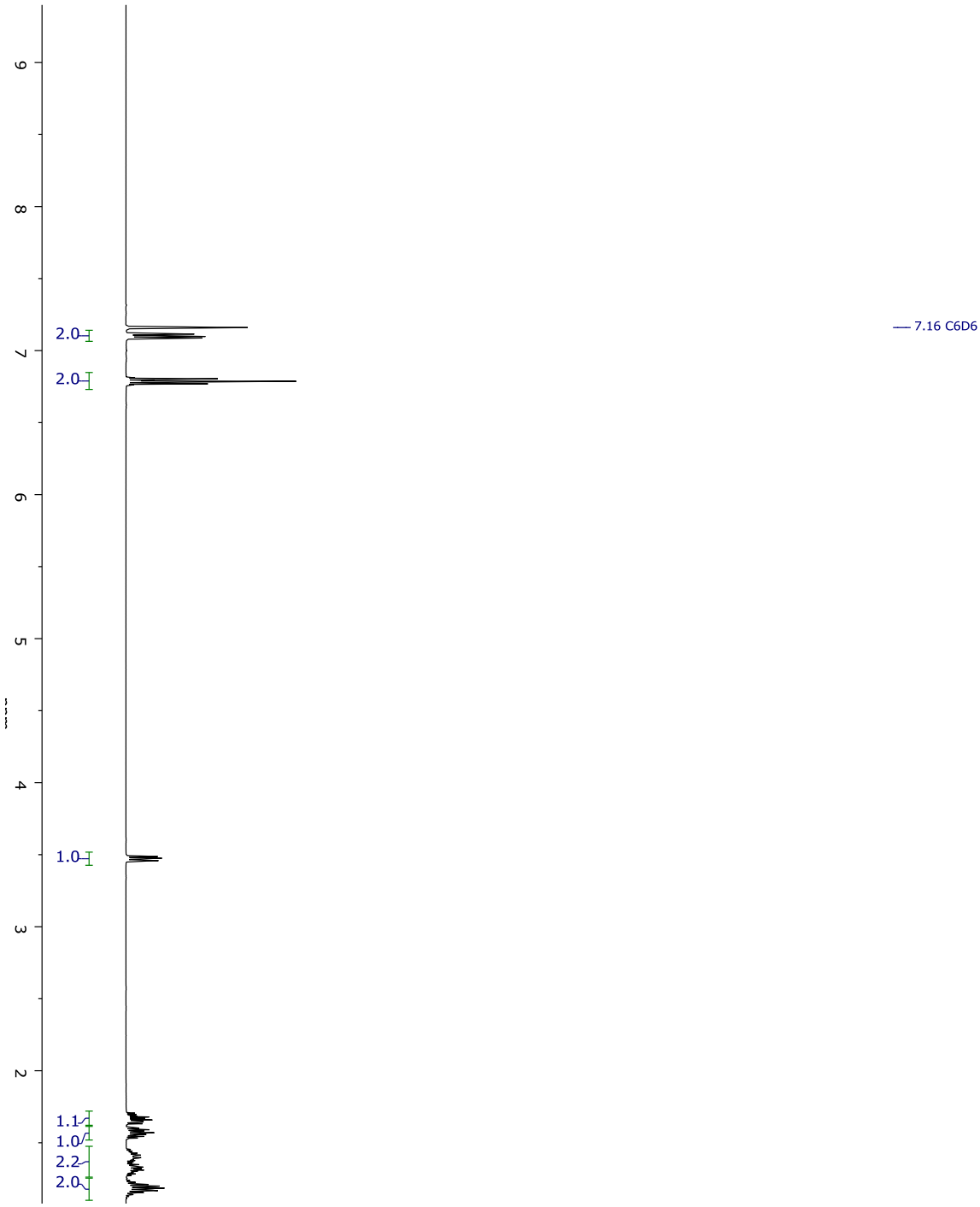
9
8
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2.0
1.0
1.1
1.0
2.2
2.0
7.16 C6D6